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המועצה המדעית לישראל

BULLETIN
OF THE
RESEARCH COUNCIL OF ISRAEL

Bull. Res. Counc. of Israel

WEIZMANN MEMORIAL ISSUE

VOLUME III JUNE-SEPTEMBER 1953 NUMBER 1-2
(Issued November 1953)

JERUSALEM

BULLETIN OF THE RESEARCH COUNCIL OF ISRAEL

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Every paper must be accompanied by a brief but comprehensive summary. Although the length of the summary is left to the discretion of the author, 3% of the total length of the paper is suggested.

(cont'd on inside back cover)

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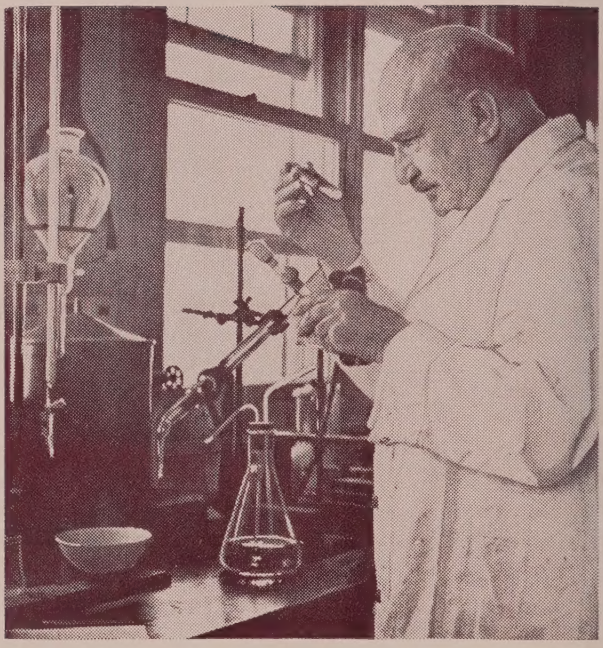
(Photo Schleisner, Rehovot)



DR. WEIZMANN'S SCIENTIFIC WORK

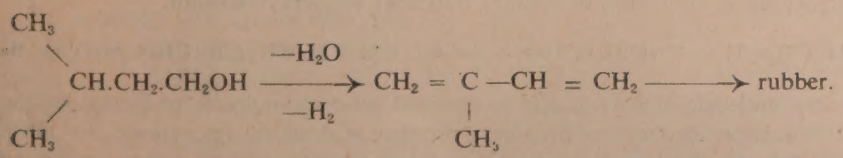
ERNST D. BERGMANN

One of the outstanding features of Weizmann's scientific life is the constancy with which he pursued his chosen subjects, the same singleness of purpose which was also characteristic of his political activities. In every field in which he has worked, he returned again and again, in spite of the interruptions necessitated by his other duties, to his original theme. We will try to show how this feature makes the description of Weizmann's scientific achievement the picture of a full and well rounded life.

1. FERMENTATION

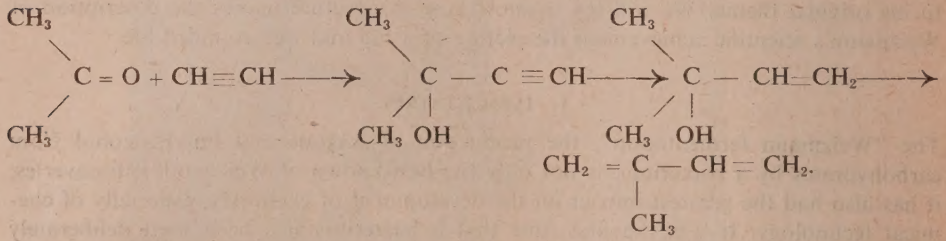
The "Weizmann fermentation", the production of acetone and butyl alcohol from carbohydrates by a bacterium, is not only the best-known of Weizmann's discoveries, it has also had the greatest impact on the development of chemistry, especially of chemical technology. It was the first time that a bacterium has been used deliberately as a tool for the production of chemicals on a technical scale — the alcoholic fermentation which has been known since prehistoric times (and which is not caused by a bacterium in the strict sense of the word) has undoubtedly been discovered accidentally — and since Weizmann's discovery many fermentations have been developed into technical processes. It was also the first time that a new raw material appeared on the horizon of chemical industry — after coal and petroleum, the carbohydrates. Weizmann has been well aware of the implications of his discovery, which is based on a raw material truly inexhaustible, in the same sense as the synthetising power of the green plants is inexhaustible, and which — if logically applied — would enable agricultural countries, poor in mineral resources, to compete in the production of chemicals. Indeed, acetone and butyl alcohol — and the ethyl alcohol formed together with them in minor quantities — are potentially identical with those hydrocarbons (ethylene, propylene, the butylenes and the butanes) which form the basis of the modern petrochemical industry.

The search for the bacterium was motivated by the desire to produce, by a fermentation process, isoamyl alcohol and from it isoprene and further, by polymerisation, a synthetic rubber:



Harries had just shown that rubber is — at least formally — a polymer of isoprene, and the increasing demand for natural rubber made the study of the possibility of a synthetic substitute appear attractive. The practical success of Weizmann's discovery

did not lie in the field of synthetic rubber: acetone became important in the first World War as an ingredient in the manufacture of smokeless powder, and butyl alcohol in the twenties as the starting materials for the lacquers which the rapidly growing automobile industry required. However, Weizmann did not lose sight of his initial objective: he studied the conversion of butyl alcohol *via* butylene into butadiene and tried — unsuccessfully — to polymerise the latter to an analog of rubber. In the second World War, he returned to the subject again, and basing himself on some prior observations, worked out a method for the production of isoprene from acetone: the condensation of the latter with acetylene affords 3-methyl-butyn-3-ol, which is half-hydrogenated to 3-methyl-buten-3-ol; dehydration of this compound leads to isoprene:



There has hardly been a chemical reaction which Weizmann and his collaborators have not applied to acetone and butyl alcohol. The conversion of *butylene* by hydration (to *sec.* butyl alcohol) and dehydrogenation to methyl ethyl ketone, and the catalytic polymerisation of butylene to high-molecular hydrocarbons of lubricating oil properties are but two examples of these investigations. A special study was devoted to the mechanism of a reaction discovered by Guerbet, through which alcohols are converted to alcohols of double and triple number of carbon atoms, under the influence of the alkoxides of sodium or calcium. The result of this research can be summarised as follows: The alkoxides decompose at elevated temperature (about 280°, *i.e.*, in the case of butyl alcohol, under pressure) to afford the corresponding aldehydes:

$$CH_3.\ CH_2\ .CH_2\ .CH_2.\ ONa \longrightarrow CH_3.\ CH_2.\ CH_2.\ CHO$$

The butyraldehyde so formed undergoes self-condensation to 2-ethyl-hex-2-enal

$$2\ CH_3.\ CH_2.\ CH_2.\ CHO \longrightarrow CH_3.\ CH_2.\ CH_2.\ CH\ =\ C\ (C_2H_5).\ CHO$$

and the latter is reduced by a third molecule of butyl alcohol (which, in the course of the reaction, is converted to sodium butyrate) to 2-ethyl-hexanol:

$$CH_3.CH_2.CH_2.CH\ =\ C\ (C_2H_5).CHO \longrightarrow CH_2.CH_2.CH_2.CH_2.CH(C_2H_5).CH_2OH.$$

Indeed, one molecule of butyric acid is obtained for each molecule of 2-ethyl-hexanol formed. The latter alcohol has become a product of practical importance (for plasticisers); moreover, the logical application of the reaction scheme makes available a number of other interesting alcohols; thus, from butyl and benzyl alcohol, 2-benzyl-butanol, and from butyl alcohol and cyclohexanol 2-butyl-cyclohexanol can be obtained:

(I) $C_6H_5.CH_2OH \longrightarrow C_6H_5CHO$

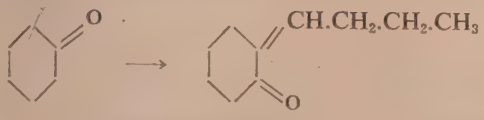
$CH_3.CH_2.CH_2.CH_2OH \longrightarrow CH_3.CH_2.CH_2.CHO$

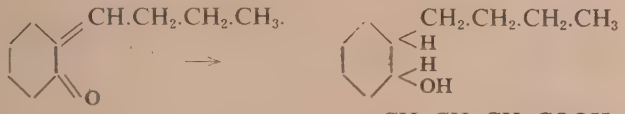
$C_6H_5.CHO + CH_3.CH_2.CH_2.CHO \longrightarrow C_6H_5.CH = C(C_2H_5).CHO$

$CH_3.CH_2.CH_2.CH_2OH + C_6H_5.CH = C(C_2H_5).CHO \longrightarrow C_6H_5.CH_2.CH(C_2H_5).CH_2OH + CH_3.CH_2.CH_2.COOH.$

(II)

$CH_3.CH_2.CH_2.CH_2OH \longrightarrow CH_3.CH_2.CH_2.CHO$

$CH_3.CH_2.CH_2.CHO +$ 

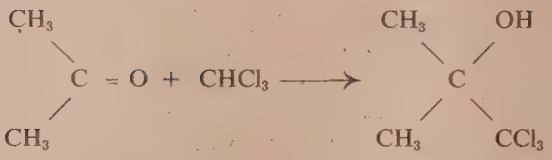
$CH_3.CH_2.CH_2.CHOH +$ 

$+ CH_3.CH_2.CH_2.COOH.$

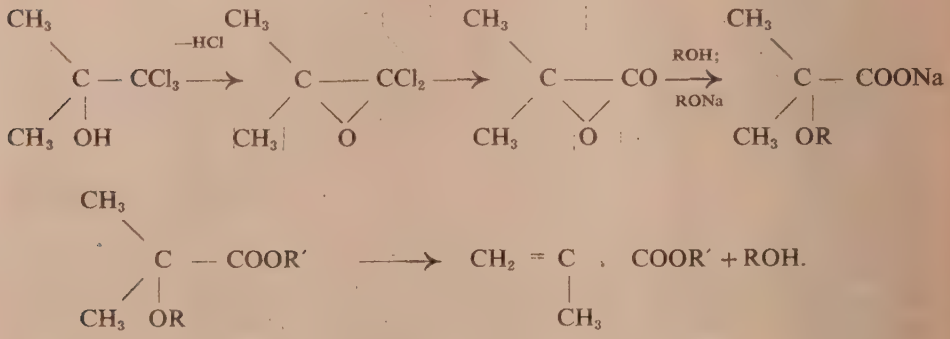
In the field of *acetone chemistry*, the reaction of acetone with acetylene has already been briefly mentioned. It had been known before, but the experimental conditions under which it had been carried out had been somewhat cumbersome. The new method applied was based on the observation of Zeltner and Genas that potassium hydroxide, activated by specific solvents, much as acetals, ketals and the dialkylethers of glycols, absorbs acetylene avidly and gives — successively — potassium mono- and di-acetylide, *e.g.*:

$$CH \equiv CH + KOH \longrightarrow CH \equiv CK + H_2O.$$

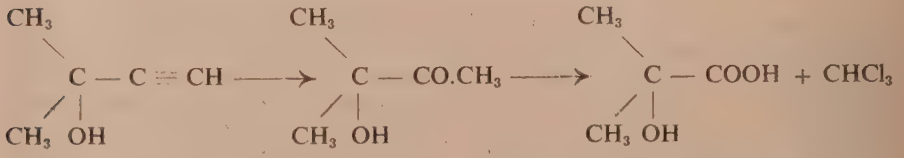
The acetylides thus formed then react with ketones and some aldehydes (those which are not too easily resinified by the excess of the potassium hydroxide present) to give acetylenic alcohols and glycols. The many reactions of which these interesting compounds are capable have been very extensively studied by Weizmann and his collaborators, and equally, further uses of the curious system potassium hydroxide—acetal have been investigated. This system acts as catalyst in the Michael reaction and in the condensation of reactive methylene and methine groups with alkyl halides and carbonyl compounds; it has also been found effective in the condensation of chloroform with aldehydes and ketones to give secondary and tertiary trichlorocarbinols, *e.g.* with acetone trichloro-*tert.* butylalcohol (acetone-chloroform, chloretone):



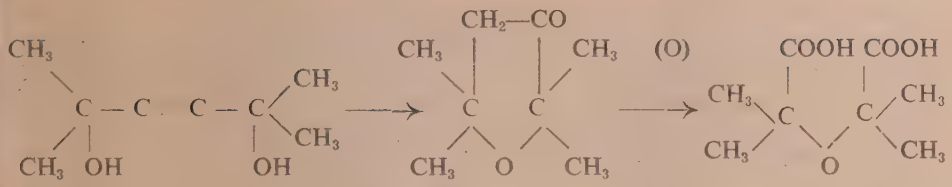
The latter should be an ideal starting material for the preparation of methacrylic acid, as it is the *ortho*-chloride of α-hydroxyisobutyric acid from which the unsaturated acid is being made. However, its hydrolysis gives only very small yields of the hydroxy-acid, which is accompanied by a number of degradation products. The difficulty could be overcome by an elegant detour. Solutions of alkali alkoxides (or of alkali hydroxides) in alcohols convert the trichloro-*tert.* butyl alcohol in satisfactory yield into the salts of the corresponding α-alkoxy-isobutyric acids; their esters are converted with practically quantitative yield into alkyl methacrylates either catalytically or by heating in presence of phosphorus pentoxide. The following plausible mechanism has been suggested for this sequence of reactions:



In order to illustrate the potentialities of the reaction between acetone and acetylene, it should be mentioned that it opens two other attractive routes into the series of α-hydroxyisobutyric and, therefore, of methacrylic acid: Hydration of 3-methyl-butyn-3-ol affords 3-methyl-butan-3-ol-2-one which can be converted by means of hypochlorite into α-hydroxyisobutyric acid (and chloroform):



1,1,4,4-Tetramethyl-butyne-1,4-diol, the product obtained by interaction of one mole of acetylene with *two moles* of acetone, is isomerised under hydrating conditions into 2,2,5,5- tetramethyl-3-keto-tetrahydrofuran, and this can be oxidised to the ether anhydride of α-hydroxyisobutyric acid:



Over the many fascinating possibilities of the chemistry of acetone and butyl alcohol, the biochemical aspects of the fermentation have not been neglected, although a study was devoted to them only many years after the original discovery. It was found that the bacterium (*Clostridium acetobutylicum* Weizmann) requires as growth factors asparagine, biotine and a third compound which was identified by other research workers in the field as *p*-aminobenzoic acid; the bacterium, therefore, belongs to the class of microorganisms which are inhibited by sulfa-drugs .The *p*-aminobenzoic acid can be replaced by a number of analogous compounds, most effective amongst them *p*-aminophenylalanine, and the bacterium would thus appear to be an interesting subject for the study of metabolic antagonisms.

The investigation of the enzyme systems involved in the acetone-butyl alcohol fermentation also revealed a number of important features. The bacterium has a very great reducing power; it converts, *e.g.*, fatty acids into the corresponding primary alcohols. The enzyme involved, undoubtedly, differentiates the bacterium from the analogous microorganisms which ferment carbohydrates to fatty acids, especially acetic and butyric acid. Furthermore, the organism is strongly pectinolytic; indeed, it is one of the bacteria — if not the most important one — which constitute the flax-retting microflora. It should also be mentioned, that under specific conditions, viz. in a completely iron-free medium, the bacterium synthetises — as a by-product of the fermentation — large quantites of vitamin B_2 (riboflavin). It would appear that certain oxidation reactions in the metabolism of this anaerobic bacterium, which are normally catalysed by iron-containing enzymes (e.g. of porphyrin character) require in the absence of the metal, vitamin B_2 as an alternative catalyst, a phenomenon which has not found the attention it deserves.

In particular, *Clostridium acetobutylicum* is characterised by the presence of powerful proteolytic and saccharolytic enzymes. As a matter of fact, the practical success of the bacterium was largely based on the fact that starchy materials could be directly *i.e.* without prior hydrolysis, subjected to fermentation. It is for this reason that Weizmann has studied very extensively the fermentability of a wide variety of natural substances, amongst them straw, wood hydrolysate and even molasses. Molasses have proven to be extremely refractory unil Weizmann, assuming that this difficulty was due to the presence of toxic substances which prevent the propagation of the initial bacterial inoculum, invented a method of "mass inoculation" which solved the problem: the initial inoculum was so strong that it could survive the toxic effects and propagate freely.

The fundamental results to which these studies have led, as well as the practical success of the acetone-butyl alcohol fermentation are sufficient reason for the constant search for other, similar bacteria to which Weizmann returned again and again. En-

richment cultures were made from natural bacterial habitats and the anaerobic bacteria present in them isolated in pure culture and investigated. None of them proved to be of practical interest, but the work done in this field represents a valuable and lasting contribution to our knowledge of the bacteria of the *butylicus* and *butyricus* type, those fascinating organisms which convert not only the hexoses into compounds containing three and four carbon atoms, but are capable — in contradistinction with most other bacteria — to accomplish the same transformation of sugars which contain only five carbon atoms.

2. OTHER BIOCHEMICAL SUBJECTS

Not only in the research on fermentation has Weizmann left the domain of classical, synthetic chemistry. In every period of his scientific life, he has devoted some attention to the amino-acids and proteins. He was one of the first to utilise the alkylation of diethyl phthalimidomalonate for the synthesis of amino-acids (he thus prepared tyrosine and 3,4-dihydroxyphenylalanine) and analogously condensed diethyl α, δ-dibromoadipate with potassio-phthalimide to yield — eventually — α, δ-diamino-adipic acid. By condensation of α-bromoacyl halides with glucosamine hydrochloride and subsequent treatment of the *N*- (α-bromoacyl)-glucosamines with ammonia, he prepared the *N*-(α-amino-acyl)-glucosamines which were obtained in the form of anhydrides and considered as model substances for the glycoproteins. A particularly interesting problem appeared to Weizmann to lie in the question of whether peptides containing unnatural amino-acids would be split by enzymes in the same manner as the natural peptides — a problem, indeed, which only recently has been revived. Thus, Weizmann prepared, starting from lauric acid and nonoic acid, via the α-bromoacyl-amino-acids, the α-amino-lauroyl and α-amino-nonoyl derivatives of alanine, valine, leucine and asparagine and in leucyl-(α-amino-nonoyl)-glycine even a tripeptide. He stated briefly that substances of this type are indeed attacked by some proteolytic enzymes.

Not only the synthesis, but also the hydrolysis of protein-type substances has been studied by Weizmann and his co-workers. After an unsuccessful attempt to improve upon Emil Fischer's classical method of protein hydrolysis, he turned to proteolytic enzymes, following a suggestion by Richard Willstaetter. The problem he set himself was the transformation of the denaturated waste protein of the vegetable oil industry, of technical fermentations and other sources (such as slaughter house wastes) into edible, i.e., biologically available proteinic food. This seemed possible if these denaturated materials could be digested outside the human body and thus be converted into amino-acids; indeed, such proteolysis products were expected to be quite palatable, as one of the amino-acids formed would invariably be glutamic acid. And again, Weizmann turned to microorganisms as the sources of such proteolytic enzymes. A fair number of bacteria and fungi was tested, but none proved equal to yeast in its proteolytic power. If yeast is plasmolysed, *e.g.* by means of ethyl acetate, and the cell juice kept at a well-defined pH, the proteolytic enzymes of the yeast are liberated, capable of breaking down quickly and efficiently any protein supplied to them; a solution of amino-acids is formed which is then used either as a liquid concentrate or as a dry powder. As in the course of the process the yeast also digests itself, the — hydrolysed — proteins of the yeast (and the other biologically active compounds it contains) are added to those of the main protein digested. An alternative method for the

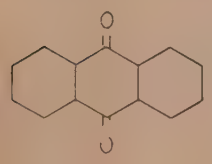
initial plasmolysis of yeast consists in its treatment with highly concentrated sugar solutions; thus, a product is obtained which combines carbohydrates with hydrolysed, well-digestible protein.

As in the case of the acetone-butyl alcohol fermentation, the practical implications of this process are fairly obvious: From vegetabilic materials — and waste material, at that — a protein substitute of meat-like qualities is obtained. Although this process has not found the acclaim Weizmann had hoped for, one wonders whether it should not be considered more seriously now that the recent investigations of Slade and McGowan have shown how wasteful the method is by which we feed the waste protein to animals and recover less than 10% of it in form of the animalic protein to which we are so accustomed.

3. POLYCYCLIC COMPOUNDS

Weizmann has been initiated into chemical research by Liebermann, who at that time was engaged in his classical studies on the structure of alizarin and its synthesis, and he has followed loyally the lead given him in the beginning of his career. He expected that the hydroxy-derivatives of the higher homolog of anthraquinone (I), naphthacenequinone (II), would be equally interesting dyestuffs. This hope has not been fulfilled: it has been realised only much later — through the experiments of L. F. Fieser — that naphthacenequinone (II) is neither in its structure nor its behaviour an analog of anthraquinone (I). Nevertheless, we owe to the systematic study of Weizmann and his colleagues a substantial part of our knowledge of the chemistry of naphthacene.

Weizmann assumed that 9-hydroxy-10,11-naphthacenequinone (III) would be similar to alizarine (IV) and that III would be formed by the usual condensation of phthalic anhydride and α-naphthol—as indicated in the formula. This reaction, however, succeeded only when as condensing agent boric acid was employed — thus, using a reagent developed a short time before by German chemists. Only then was the keto-acid (V) formed — instead of the undesirable fluoran derivatives (VI) — which could



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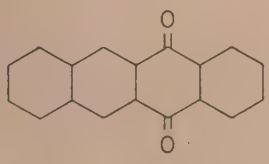

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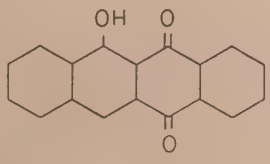

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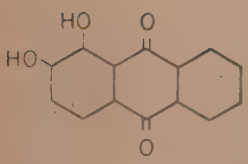

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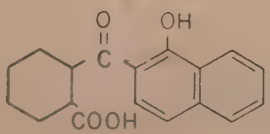
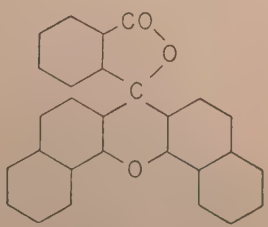


V



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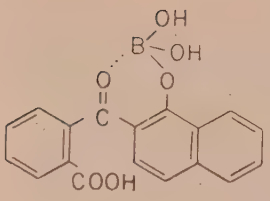

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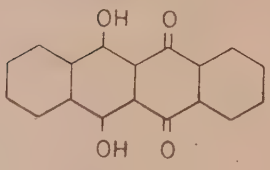

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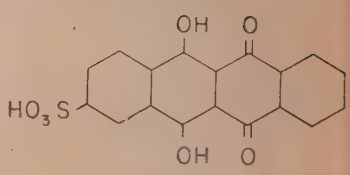

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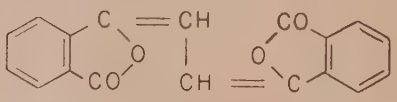


X

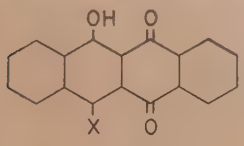
easily be cyclised to III. Many years after this discovery, Weizmann formulated correctly the mechanism of the reaction: formation of an inner-complex boric ester (VII) stabilises V and prevents it from reacting further with α-naphthol to give VI. If the ring closure of V is carried out under more stringent conditions, sulfonation of III takes place or oxidation to 9,12-dihydroxy-10,11-naphthacenequinone (VIII); here, indeed, we have a certain analogy to the behaviour of α-hydroxy-anthraquinones. In the end, VIII is sulfonated to a sulfonic acid, formulated as IX.

The quinone VIII had been obtained before, *viz.* by isomerisation of the so-called "ethine-diphthalide", the product (X) of the condensation between phthalic anydride and succinic anhydride. The identity of these compounds as well as the reductive conver- of IV into naphthacene established the firm basis of this whole reaction scheme.

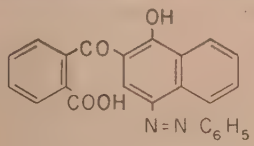
When V was treated with phosphorus pentachloride, the hydroxyl was replaced by chlorine, and subsequent cyclisation gave 9-chloro-10,11-naphthacenequinone; bromination of V was — justly — assumed to affect the 4-position of the naphthalene nucleus so that the cyclisation product would be XI (X = Br). Similar substances (X = NO_2, Cl) are obtained by mononitration or chlorination of III: reduction and replacement of the amino-group in XI (X = NH_2) by hydroxyl afford VIII. The amino-compound XI (X = NH_2) could also be obtained by condensation of V with benzene-diazonium chloride (to XII), reductive fission to the 4-amino-derivative of V and cyclisation (by means of heating in nitrobenzene).

When it became clear that these first derivatives of naphthacenequinone had no dyestuff properties, Weizmann attempted to achieve his aim by the synthesis of more highly hydroxylated compounds. In the course of these studies, a useful synthesis of 4-hydroxyphthalic anhydride (XIII) was elaborated, by sulfonation of phthalic anhydride with fuming sulfuric acid at 200° and subsequent treatment of the sulfonic acid formed with sodium hydroxide at 175-180°; less easy proved the preparation of 3-methoxyphthalic anhydride (XIV) by permanganate oxidation of 1-methoxy-5-hydroxynaphthalene (XV). Condensation of XIV with α-naphthol led to the formation of XVI or XVII, and was, therefore, accompanied by demethylation — indeed, the affinity of neighbouring hydroxy-groups to the carbonyls of naphthacenequinone

or of V (hydrogen bridge) is the reason for the often observed demethylation in reactions in which *ortho*-alkoxyl derivatives of these compounds are expected. The keto-acid (XVI or XVII) could be cyclised to XVIII or XIX, and the same sequence of reactions converted 4-hydroxy-phthalic anhydride (XIII) into the quinone XX or XXI. Equally, from hemipinic anhydride (XXII) with α-naphthol, a quinone (XXIII or XXIV), and with 1,4-dihydroxy-naphthalene, the quinone XXV was obtained, and a few more reactions were carried out with 1,4- and 1,5-dihydroxynaphthalene, respectively. It should be noted that the demethylated quinones XXIII (or XXIV) and XXV are, indeed, dyes, but not vat dyes, they are analoga of alizarin, thus lac dyes.



XI



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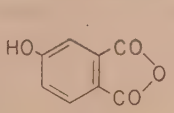

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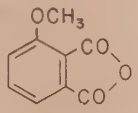

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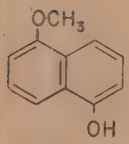

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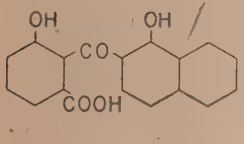

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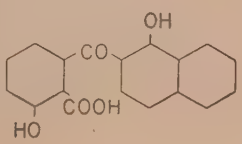

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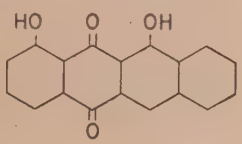

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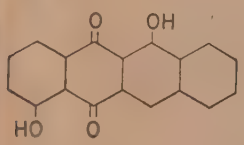

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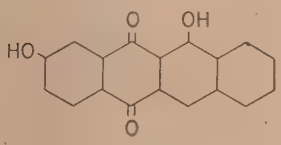

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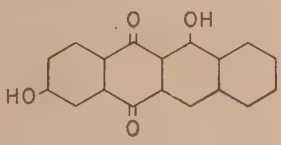
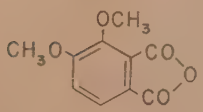


XXI



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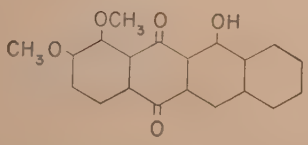

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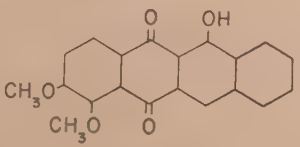

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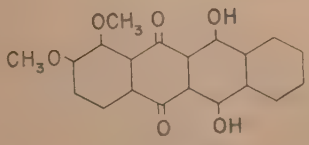
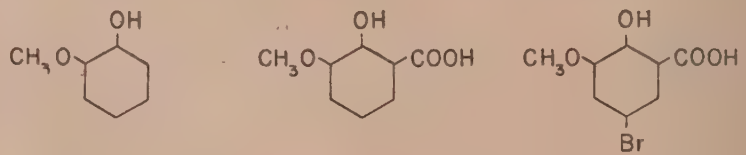


XXV

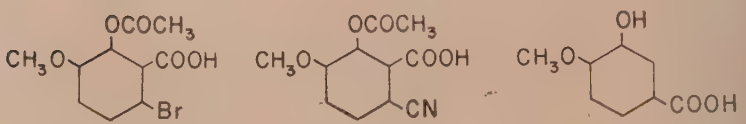
These were not the only condensations of α-naphthols with phthalic anhydrides, which have been carried out by Weizmann and his co-workers, nor remained the fruitful boric acid method limited to the synthesis of hydroxy-naphthacenequinones. A large series of anthraquinone derivatives became available through analogous reactions of phthalic anhydrides with monocyclic phenols and their derivatives. Thus,

phthalic anhydride was condensed with the three cresols and their methyl ethers, 2,4-dimethylphenol and pyrogallol trimethyl ether, 4-hydroxy-phthalic anhydride with the three cresols, 2,4-dimethyl-phenol and its methyl ether, 4-methoxyphthalic anhydride with the methyl ethers of *p*-cresol and 2,4-dimethylphenol, and hemipinic anhydride with veratrol and pyrogallol trimethyl ether.

It is characteristic for Weizmann's perseverance that for many years he tried to round off these studies by devising a method for the synthesis of hemipinic anhydride — in the early investigations reported here, he used a product obtained by degradation of suitable natural alkaloids. One of his last publications is devoted to an interesting new, though unsuccessful approach to the problem. The attempt to connect hemipinic acid anhydride (XXII) with guaiacol (XXVI) through 2-hydroxy-3-methoxy-benzoic acid (XXVII), which can be easily obtained from the former by Kolbe's synthesis, was based on the experience that hydroxy-groups in the benzene ring have a greater directive power for further substitution than methoxy-groups, but that the latter are more effective than acylated hydroxyls. Indeed, the acid XXVII afforded, on bromination, 2-hydroxy-3-methoxy-5-bromobenzoic acid (XXVIII), whilst the *O*-acetyl derivative of XXVII yielded under the same conditions 2-acetoxy-3-methoxy-6-bromobenzoic acid (XXIX). Unfortunately, the replacement of the bromine atom in this last acid by the nitrile group, which was expected to give the hemipinic acid derivative XXX, was accompanied by decarboxylation, and isovanillic acid (XXXI) was obtained.

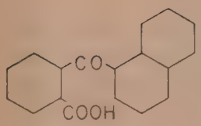


XXVI XXVII XXVIII



XXIX XXX XXXI

Whilst the studies in the polycyclic series reported so far have had no practical consequences, another method which Weizmann has investigated briefly in the early years of the century and more extensively more than thirty years later, has found much wider use, *viz.* the interaction of phthalic anhydrides with aromatic Grignard compounds which equally leads to keto-acids of type V and further to polycyclic quinones, both of unambiguous atructure. If a Grignard compound such as α- or β-naphthylmagnesium bromide is added to phthalic anhydride ("inverse Grignard reaction", in which the second component is always kept in excess) the keto-acids XXXII and XXXIII are formed which are easily cyclised to 1,2-benzanthraquinone(XXXIV) and naphthacenequinone (XXXV), respectively. The wide range of polycyclic substances so available is obvious — with 9-phenanthrylmagnesium bromide, *e.g.*, 1,2,3,4-dibenzanthraquinone (XXXVI) is obtained, and the value of the method becomes even more remark-



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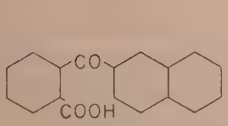

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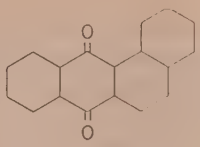

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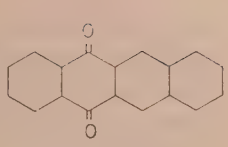

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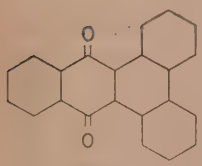

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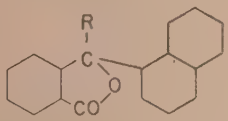
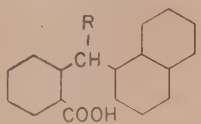


XXXVII



XXXVIII

able if one adds that many aliphatic and hydroaromatic succinic anhydrides — though not all of them — are apt to give analogously γ-keto-acids.

The usefulness of the method was yet further enhanced by the investigations of L.F. Fieser who found that — in accordance with prior observations on similar substances — the esters of these keto-acids react with alkylmagnesium bromides preferentially at the keto-group, affording lactones of type XXXVII and, by reduction of the latter, substituted 2-benzyl-benzoic acids, such as XXXVIII. These have become important as the starting materials for the many methylated polycyclic hydrocarbons which are — actually or potentially — carcinogenic. Thus — again — has Weizmann's work led from organic chemistry to a field of great *biological* importance.

4. THE AROMATISING CRACKING PROCESS

It is perhaps not wholly accidental that the last major piece of work which Weizmann has carried out consisted in the elaboration of a process for the production of the whole gammut of aromatic hydrocarbons from petroleum or similar hydrocarbonaceus materials (natural gas, shale oil, the coal-oil of low-temperature carbonisation of coal). It had been known for some time that at high temperatures, petroleum fractions show a substantial increase in aromaticity; however, neither the practical implications of this phenomenon nor its mechanism had been given particular attention. In experiments with local shale oil, the chemists of the Sieff Institute had observed that treatment of the material at high temperatures with metals (which were expected to renove the sulphur contained in the oil in form of organic sulphur compounds) resulted in the formation of a product rich in aromatic hydrocarbons. This effect was quickly found not to be limited to shale oil and not to be dependent on the action of the metals; it could be duplicated with any hydrocarbonaceous materials at a suitable temperature. Indeed, at temperatures of about 650—700° and — practically — atmospheric pressure, these materials are converted, to about an equal extent, into a mixture of almost pure aromatic hydrocarbons and hydrocarbon gases, mostly of unsaturated character. Independently of the composition of the charging stock, the aromatics consisted of the whole series of hydrocarbons from benzene upwards to the most complicated polycyclics (including the carcinogenic 3,4-benzpyrene), and any sulphur or nitrogen

contained in the charging stock, reappeared as hydrogen sulfide and ammonia, respectively, in the gaseous products of the reaction. This latter feature of the product represents an important advantage over the classical source of aromatic hydrocarbons, coal tar, whilst its former property represented a distinct improvement in comparison with the other process for the production of aromatic hydrocarbons from petroleum which at that time entered the field of industrial petrochemistry, the cyclo-dehydrogenation of paraffins: this method gives aromatics of the same number of carbon atoms as the starting material.

When the production of aromatic hydrocarbons became of importance for the War Effort during the Second World War, these observations were elaborated by Weizmann and his co-workers into a large-scale process which, however, found practical application (under the name "Catarol" process) only after the end of the War. Its value lies in the fact that petroleum is not longer a raw material for the production of fuel, but the starting point for the synthetic-chemical industry: the process affords in one step all the hydrocarbons on which the chemical synthesis relies to-day. Nevertheless, the fuel value of the aromatic hydrocarbons now available was also studied by Weizmann and his group, which included the chemists and engineers of Messrs. Manchester Oil Refinery in Manchester, England. These hydrocarbons are characterised by unusually high octane numbers and can, therefore, serve as aviation fuel ingredients. It is true that they tend to form finely divided carbon as one of the combustion products; but also this difficulty can be overcome by their combination with compounds such as methylethylketone or methyl*iso*butylketone which catalyse the complete combustion of hydrocarbons (to carbon dioxide and water) and have, moreover, themselves octane numbers between 100 and 120. Such mixed fuels have been tested with a fair measure of success and may constitute an interesting possibility for the future development of compression engines.

It was only natural that Weizmann took a great interest in the elucidation of the chemical composition of the aromatisation product, especially of its polycyclic fractions. As already pointed out, almost all the parent hydrocarbons of the polycyclic series were isolated from the product and together with them a number of substances of the biphenyl and binaphthyl type, obviously formed by bimolecular dehydrogenation of simple aromatic hydrocarbons at the elevated temperature. Of the substituted aromatic systems, practically only methyl and vinyl derivatives (styrene type) are present; this could be shown to be due to the pyrolysis of higher alkyl-aromatics which proceeds by one of the three following general schemes:

$$\text{(a)}\quad \text{Ar.}\ CH_2CH_2CH_2R \longrightarrow \text{Ar.}\ CH_3 + R.CH{=}CH_2$$
$$\text{(b)}\quad \text{Ar.}\ CH_2CH_2CH_2R \longrightarrow \text{Ar.H} + R.CH_2CH{=}CH_2$$
$$\text{(c)}\quad \text{Ar.}\ CH_2CH_2CH_2R \longrightarrow \text{Ar.}CH{=}CH_2 + CH_3R.$$

It is interesting to recall that also in the second aromatisation process, based on cyclodehydrogenation, the methyl group is vastly favoured as a side-chain. In this case, however, Herington and Rideal have shown that the phenomenon is due to the mechanism of dehydrogenation of the initial paraffin, which affects the terminal C-C bond; the olefin R. $CH = CH_2$ is then cyclo-isomerised so that the carbon atom No. 2 becomes a member of the ring, whilst C_1 remains as methyl group.

The observations on the composition of the aromatisation product together with the study of the kinetics of its formation have led to the following mechanism for the high-temperature cracking of hydrocarbon oils: All the larger molecules are converted into small ones, mainly of unsaturated character, ethylene, propylene, the butylenes and especially butadiene. In the second stage of the process, butadiene disappears again by a diene reaction with the olefinic gases which leads to cyclohexene derivatives — a reaction which for butadiene and ethylene has been known to occur:

In the third and last stage, the hydroaromatic systems are dehydrogenated to the corresponding aromatic ones; at the high prevailing temperature, the latter are thermodynamically favoured. The process is, thus, a purely thermal one; indeed, at these high temperatures, no catalytic effects can be expected; and the role of the metals on the system is that of heat transfer media only.

It is obvious from the mechanism outlined above, that for naphthenic oils the aromatising cracking will be accompanied by direct dehydrogenation to the compounds (third stage); with this limitation, the mechanism explains that the composition of the final product is independent of that of the charging stock.

The hypothesis of a thermal diene synthesis is of importance not only for the understanding of high-temperature cracking of hydrocarbon oils; it is not impossible that also the aromatic hydrocarbons of the coal tar are not — or not only — formed by disintegration of the graphite structure (in which the polycyclic systems appear to be preformed), but also by a succession of breakdown and re-synthesis. In any event, the phenomena observed in the process of aromatising cracking open a new and fruitful field for further research both to the organic and the physical chemist.

These pages represent an attempt to re-draw the general lines of Weizmann's scientific work. It is almost impossible to do more than that in the limited space that is at the disposal of this essay. However, the reader will be able to get a picture of Weizmann's wide interests in the field of chemistry from the impressive list of his papers and patents appended to this general survey.

DR. WEIZMANN'S SCIENTIFIC PUBLICATIONS

1903

1. Chr. Deichler and Ch. Weizmann, Studies and syntheses in the naphthacenequinone series, Part I, *Ber.*, **36**, 547.
2. Chr. Deichler and Ch. Weizmann, Studies and syntheses in the naphthacenequinone series, Part II, *Ber.*, **36**, 719.
3. Chr. Deichler and Ch. Weizmann, Studies and syntheses in the naphthacenequinone series, Part III, *Ber.*, **36**, 2326.

1904

4. S.Sh. Pickles and Ch. Weizmann, The action of anhydrides on organomagnesium compounds, Part I. The action of phthalic anhydride on α-naphthylmagnesium bromide, *Proc. Chem. Soc.*, **20**, 201.
5. S. Sh. Pickles and Ch. Weizmann, The halogen derivatives of naphthacenequinone, *Proc. Chem. Soc.*, **20**, 220.

1905

6. J. Q. Orchardson and Ch. Weizmann, Some derivatives of naphthoyl-benzoic acid and of naphthacenequinone, *Proc. Chem. Soc.*, **21**, 307.
7. Ch. Weizmann and E. B. Falkner, Ethyl β-naphthoyl-acetate, *Proc. Chem. Soc.*, **21**, 307.

1906/7

8. J. Q. Orchardson and Ch. Weizmann, Some derivatives of naphthoyl-benzoic acid and naphthacenequinone, *J. Chem. Soc.*, **89**, 115.
9. Ch. Weizmann and E. B. Falkner, Ethyl β-naphthoyl-acetate, *J. Chem. Soc.*, **89**, 122.
10. W. H. Perkin, Ch. Weizmann, H. L. Smith, N. A. Creeth, W. H. Haworth, J. Naylor and V. J. Harding, Some derivatives of catechol, pyrogallol, benzophenone and of substances related to natural dye-stuffs, *Proc. Chem. Soc.*, **22**, 269; *J. Chem. Soc.*, **89**, 1649.
11. W. H. Bentley and Ch. Weizmann, 4-Hydroxyphthalic acid and 4-methoxyphthalic acid, *Proc. Chem. Soc.*, **22**, 323; *J. Chem. Soc.*, **91**, 98.
12. W. H. Bentley, R. Robinson and Ch. Weizmann, 3-Hydroxyphthalic acid, 3-methoxyphthalic acid and their derivatives, *Proc. Chem. Soc.*, **23**, 323; *J. Chem. Soc.*, **91**, 104.
13. W. H. Bentley, A. Friedl, F. Thomas and Ch. Weizmann, Derivatives of naphthacenequinone, *Proc. Chem. Soc.*, **22**, 324.
14. W. H. Bentley, A. Friedl, Ch. Weizmann, F. Thomas, E. C. C. Baly and W. B. Tuck, Derivatives of naphthacenequinone, *J. Chem. Soc.*, **91**, 411.
15. A. Friedl, Ch. Weizmann and M. Wyler, Fluoresceines and eosines of 4-hydroxyphthalic acid, 4-methoxyphthalic acid and hemipinic acid, *J. Chem. Soc.*, **91**, 1584.
16. W. H. Bentley, A. Friedl and Ch. Weizmann, Derivatives of naphthacenequinone, *J. Chem. Soc.*, **91**, 1588.
17. W. H. Bentley, H. D. Gardner, Ch. Weizmann, J. H. Andrew and C. V. Temperley, Studies on anthraquinone and phthaleine, *J. Chem. Soc.*, **91**, 1626.

1908

18. W. H. Bentley and Ch. Weizmann, Studies on anthraquinone, *Proc. Chem. Soc.* **24**, 52; *J. Chem. Soc.*, **93**, 435.

1909

19. D. Harrop, R. V. Norris and Ch. Weizmann, Derivatives of naphthacenequinone, *J. Chem. Soc.*, **95**, 279.

20. D. Harrop, R. V. Norris and Ch. Weizmann, Some derivatives of anthraquinone, *J. Chem. Soc.*, **95**, 1312.

1910

21. V. J. Harding and Ch. Weizmann, $\triangle^1$-Nonylenic acid, *J. Chem. Soc.*, **97**, 299.
22. G. M. Walsh and Ch. Weizmann, 1,4-Dichloroanthraquinone and its derivatives, *J. Chem. Soc.*, **97**, 685.
23. V. J. Harding and Ch. Weizmann, Synthesis of 6-carboxy-3,4-dimethoxyphenyl-glyoxylic acid., *J. Chem. Soc.*, **96**, 1126.

1911

24. R. Alpern and Ch. Weizmann, Experiments on the preparation of glycerides of amino acids, *J. Chem. Soc.*, **99**, 84.
25. V. J. Harding, G. M. Walsh and Ch. Weizmann, β-Methyl-$\triangle^{\alpha,\lambda}$-dodecadiene and β-methyl-$\triangle^{\alpha,\gamma}$-decadiene, *J. Chem. Soc.*, **99**, 448.
26. A. Hopwood and Ch. Weizmann, Syntheses of dipeptides of α-aminolauric acid with glycine, alanine, valine, leucine and asparagine, *J. Chem. Soc.*, **99**, 571.
27. A. Hopwood and Ch. Weizmann, Synthesis of polypeptides of α-amino-*n*-nonylic acid with glycine, alanine, valine, leucine, asparagine and aspartic acid, *J. Chem. Soc.*, **99**, 1577.

1913

28. H. Stephen and Ch. Weizmann, α,γ-Derivatives of adipic and β-methyladipic acid and preparation of muconic and β-methyl-muconic acid., *J. Chem. Soc.*, **103**, 269.
29. Ch. Weizmann and A. Hopwood, Syntheses of anhydrides of α-aminoacyl-glucosamine, *Proc. Roy. Soc., London.*, **A, 88**, 455.
30. Ch. Weizmann, H. Stephen and G. S. Agashe, Condensation of acid chlorides with the ethyl esters of cyanoacetic acid and acetoacetic acid, Part I, *J. Chem. Soc.*, **103**, 1855.
31. Ch. Weizmann and G. S. Agashe, Hydrolysis of proteins with an alcoholic solution of hydrochloric acid, *Biochem. J.*, **7**, 437.

1914

32. H. Stephen and Ch. Weizmann, Derivatives of 3,4-dimethoxy-acetophenone and 4,5-dimethoxy-*o*-tolyl-methyl-ketone and the synthesis of phenyl-glyoxalines with substituents in the benzene ring, *J. Chem. Soc.*, **105**, 1046.
33. H. Stephen and Ch. Weizmann, Synthesis of d,l-tyrosine and d,l-3,4-dioxyphenyl-alanine, *J. Chem. Soc.*, **105**, 1152.
34. H. Bradbury and Ch. Weizmann, Some homologs of alizarin, *J. Chem. Soc.*, **105**, 2748.

1915

35. J. Bradshaw, H. Stephen and Ch. Weizmann, Condensation of acid chlorides with the ethyl esters of cyanoacetic acid, malonic acid and acetoacetic acid, Part II. Some experiments with ethyl phthalimino-acetoacetate and ethyl-γ-ethoxy-acetoacetate, *J. Chem. Soc.*, **107**, 803.
36. M. Copisarow and Ch. Weizmann, Phthalides of the benzene, naphthalene and carbazole series. *J. Chem. Soc.*, **107**, 878.

1920

37. Ch. Weizmann and S. F. Garrard, Some condensations of *n*-butyl alcohol and *n*-butyraldehyde, *J. Chem. Soc.*, **117**, 324.

1934

38. V. Henri, Ch. Weizmann and Y. Hirshberg, Décomposition photochimique du glycocolle, *Compt. Rend.*, **199**, 1205.

1935

39. Ch. Weizmann, E. Bergmann and F. Bergmann, Grignard reactions with phthalic anhydrides, *J. Chem. Soc.*, 1367.
40. Ch. Weizmann, O. Blum-Bergmann and F. Bergmann, The reaction of Grignard reagents with some succinic anhydrides, *J. Chem. Soc.*, 1370.

1936

41. Ch. Weizmann and E. Bergmann, Grignard reactions with ethyl β-chloropropionate, I, *J. Chem. Soc.*, 401.
42. Ch. Weizmann and E. Bergmann, Methoxylated *o*-benzoyl-benzoic acids, *J. Chem. Soc.*, 567.
43. Ch. Weizmann, E. Bergmann and Y. Hirschberg, The photochemical deamination of amino acids in water solution, Part I, *J. Amer. Chem. Soc.*, **58**, 1675.

1937

44. Ch. Weizmann, E. Bergmann and L. Haskelberg, Mechanism and applicability of the Guerbet reaction, *Chem. and Ind.*, **56**, 587.
45. Ch. Weizmann and H. Davies, Note on the butyl alcohol-acetone fermentation of maize, *J. Soc. Chem. Ind.*, **56**, 8T.
46. Ch. Weizmann and B. Rosenfeld, The activation of the butyl alcohol-acetone fermentation of carbohydrates by *Clostridium acetobutylicum* (Weizmann), *Biochem. J.*, **31**, 619.
47. E. Simon and Ch. Weizmann, Ueber die Aceton - Butylalkohol Gaerung, *Enzymologia*, **4**, 169.

1938

48. Ch, Weizmann and E. Bergmann, Polycyclic aromatic hydrocarbons, *Scripta Academica Hierosolymitana.*
49. Ch. Weizmann, Y. Hirshberg and E. Bergmann, Photochemical interaction between ketones and secondary alcohols, *Nature*, **141**, 1012.
50. Ch. Weizmann, E. Bergmann and T. Berlin, Synthesis of polycyclic compounds from dicyclohexenyl, *J. Amer. Chem. Soc.*, **60**, 1331.
51. Ch. Weizmann, E. Bergmann and Y. Hirshberg, Photochemical interaction between ketones and alcohols, *J. Amer. Chem. Soc.*, **60**, 1530.
52. Ch. Weizmann, Y. Hirshberg and E. Bergmann, The photochemical deamination of amino acids in water solution, Part II, *J. Amer. Chem. Soc.*, **60**, 1799.
53. Ch. Weizmann and F. Bergmann, Interaction between Grignard compounds and maleic acid derivatives, *J. Amer. Chem. Soc.*, **60**, 2647.

53a. Ch. Weizmann, An Ethyl Alcohol Producing Bacillus Isolated from *Hibiscus sabdariffa*, *Chem. and Ind.*, 1049.

1939

54. Ch. Weizmann, E. Bergmann and L. Haskelberg, Phenylated phthalic acids and anthracene derivatives, *J. Chem. Soc.*, 391.
55. Ch. Weizmann and E. Bergmann, 1,4,9,10-tetraphenyl-anthracene, *J. Chem. Soc.*, 494.
56. Ch. Weizmann, E. Bergmann and Y. Hirshberg, Hydrolytic deamination of amino acids, *Nature*, **143**, 723.
57. Ch. Weizmann, L. Haskelberg and T. Berlin, The boric acid synthesis of *peri*-hydroxyanthraquinones, *J. Chem. Soc.*, 398.
58. Ch. Weizmann and B. Rosenfeld, The specific nutritive requirements of *Clostridium acetobutylicum* (Weizmann) II, *Biochem. J.*, **37**, 1376.

1940

59. Ch. Weizmann, V. Henri and E. Bergmann, Identification and determination of aromatic compounds in mineral oils, *Nature*, **146**, 230.
60. E. Bergmann and Ch. Weizmann, Some syntheses of biochemical interest, *Medical Leaves*, **3**, 223.
61. Ch. Weizmann and E. Hellinger, Studies on some strains of butyric acid producing plectridia isolated from hemp, jute and flax, *J. Bacteriol.*, **40**, 665.

1944

62. Ch. Weizmann and L. Haskelberg, Attempted synthesis of hemipinic acid from guaiacol, *J. Org. Chem.*, **9**, 121.

1947

63. Ch. Weizmann, M. Sulzbacher and E. Bergmann, α-Cyclohexyl-β-propylacrylic acid from cyclohexanol, *J. Chem. Soc.*, 772.
64. Ch. Weizmann, M. Sulzbacher and E. Bergmann, Reduction of α, β-unsaturated carbonyl compounds by sodium butoxide, *J. Chem. Soc.*, 851.
65. Ch. Weizmann, E. Bergmann and M. Sulzbacher, Carbohydrates as an alternative source to petroleum for organic chemicals, *Chem. and Ind.*, 769.

1948

66. Ch. Weizmann, M. Sulzbacher and E. Bergmann, Synthesis of α-alkoxyisobutyric acids and alkyl methacrylates from acetonechloroform, *J. Amer. Chem. Soc.*, **70**, 1153.
67. Ch. Weizmann, E. Bergmann and M. Sulzbacher, Preparation of acetonechloroform and its homologs, *J. Amer. Chem. Soc.*, **70**, 1189.
68. Ch. Weizmann, E. Bergmann and M. Sulzbacher, Derivatives of salicylic acid, *J. Org. Chem.* **13**, 796.
69. Ch. Weizmann, E. Bergmann, E.F. Chandley, H. Steiner, M. Sulzbacher and E. Zimkin, Studies in selective extraction and adsorption I, *J. Soc. Chem. Ind.*, **67**, 203.
70. Ch. Weizmann, E. Bergmann, M. Sulzbacher and E. R. Pariser, Studies in selective extraction and adsorption III, *J. Soc. Chem. Ind.*, **67**, 225.
71. Ch. Weizmann, E. Bergmann, H. Steiner and M. Sulzbacher, Production of aromatic hydrocarbons from petroleum, *J. Soc. Chem. Ind.*, **67**, 114.

1950

72. Ch. Weizmann, E. Bergmann and M. Sulzbacher, Further observations on the Guerbet reaction, *J. Org., Chem.* **15**, 54.
73. Ch. Weizmann, E. Bergmann and M. Sulzbacher, The use, for condensation reactions, of potassium hydroxyde in solvents of the acetal type, *J. Org. Chem.*, **15**, 918.

1951

74. Ch. Weizmann, E. Bergmann *et al.*, The aromatizing cracking of hydrocarbon oils, I. Process data and mechanism, *Chem. and Ind. Eng.*, **43**, 2312.
75. Ch. Weizmann, E. Bergmann *et al.*, The aromatizing cracking of hydrocarbon oils, II. The polycyclic fractions, *Chem. and Ind. Eng.*, **43**, 2318.
76. Ch. Weizmann, E. Bergmann *et al.*, The aromatizing cracking of hydrocarbon oils, III. Influence of the nature of the charging stock, *Chem. and Ind. Eng.*, **43**, 2322.
77. Ch. Weizmann, E. Bergmann *et al.*, The aromatizing cracking of hydrocarbon oils, IV. Qualitative experiments on the conversion of butylene into aromatics, *Chem. and Ind. Eng.*, **43**, 2325.

DR. WEIZMANN'S PATENTS

(From the *Centralblatt* (until 1906) and the *Chemical Abstracts*)

1.	DRP 134. 986	Preparations of naphthacenequinone derivatives (*Centralblatt* 1902 II 1085).
2.	DRP 138. 324.	Preparation of dihydroxynaphthacenequinones (*Centralblatt* 1903 I 371).
3.	DRP 138. 325.	Preparation of naphthacenequinone derivatives (*Centralblatt* 1903 I 371).
4.	DRP 141, 025.	Prepararion of α-hydroxynaphthoyl-benzoic acid (*Centralblatt* 1905 I 1197).
5.	B.P. 5, 032.	Camphene (*C.A.*, 1907, **1**, 932).
6.	B.P. 8, 266.	*iso*Bornyl esters (*C.A.*, 1907, **1**, 1339).
7.	B.P. 10, 798.	*iso*Bornyl esters (*C.A.*, 1907, **1**, 1792).
8.	B.P. 18, 280.	*iso*Bornyl esters (*C.A.*, 1907, **1**, 2644).
9.	B.P. 23, 875.	*iso*Bornyl esters (*C.A.*, 1907, **1**, 2520).
10.	B,P. 23, 878.	Purifying turpentine for the manufacture of pinene hydrochloride (*C.A.*, 1907, **1**, 2837).
11.	French P. 369, 449.	Camphene (*C.A.*, 1908, **2**, 2428).
12.	DRP 197, 163.	Camphene from pinene hydrochloride (*C.A.*, 1908, **2**, 2429).
13.	U.S.P. 896, 962.	Making camphene (*C.A.*, 1908, **2**, 3263).
14.	B.P. 21, 946.	Camphor (*C.A.*, 1909, **3**, 691).
15.	B.P. 16,605.	*iso*Bornyl esters (*C.A.*, 1909, **3**, 691).
16.	U.S.P. 910,978.	*iso*Bornyl esters (*C.A.*, 1909, **3**, 1062).
17.	D.R.P. 205,849.	Camphene and *iso*Bornyl acetate (*C.A.*, 1909, **3**, 1671).
18.	D.R.P. 207,155.	Fatty acid *iso*Bornyl esters (*C.A.*, 1099, **3**, 1913).
19.	U.S.P. 1,144,217.	Dihalogen derivatives of saturated hydrocarbons. (*C.A.*, 1915, **9**, 2291).
20.	B.P. 4,845.	Acetone and butyl alcohol (*C.A.*, 1919, **13**, 1595).
21.	U.S.P. 1,315,585.	Acetone and alcohols by fermentation (*C.A.*, 1919, **13**, 282).
22.	B.P. 131,628.	Glycols (*C.A.*, 1920, **14**, 286).
23.	U.S.P. 1,329,214.	Acetone and butyl alcohol by fermentation (*C.A.*, 1920, **14**, 998).
24.	Can. Pat. 202,135.	*sec.*Butylalcohol from butenes and strong acids (*C.A.*, 1920, **14**, 2645).
25.	Can. Pat. 203,264.	Ethylmethylketone (*C.A.*, 1920, **14**, 2935).
26.	Can. Pat. 203,408.	Manufacture of hydrocarbons (*C.A.*, 1920, **14**, 2936).
27.	B.P. 149,355.	Acetone and butyl alcohol (*C.A.*, 1921, **15**, 409).
28.	B.P. 150,360.	Acetone and butyl alcohol (*C.A.*, 1921, **15**, 726).
29.	B.P. 161,591.	*sec.* Butyl alcohol (*C.A.*, 1921, **15**, 2445).
30.	B.P. 164,023.	Acetone and butyl alcohol (*C.A.*, 1922, **16**, 139).
31.	B.P. 164,366.	Fermenting starchy materials (*C.A.*, 1922, **16**, 460).
32.	B.P. 164,762.	Acetone and butyl alcohol (*C.A.*, 1922, **16**, 460).
33.	U.S.P. 1,395,620.	Naphthene hydrocarbons from butene (*C.A.*, 1922, **16**, 567).
34.	B.P. 165,452.	Hydrocarbons (*C.A.*, 1922, **16**, 1252).
35.	U.S.P. 1,408,720.	*sec.*Butyl alcohol (*C.A.*, 1922, **16**, 1593).
36.	U.S.P. 1,437,697.	Acetone and butyl alcohol by fermentation (*C.A.*, 1923, **17**, 849).
37.	B.P. 203,352.	Titanium oxide and sulfate (*C.A.*, 1924, **18**, 573).
38.	U.S.P. 1,489,183.	Treating titanium oxide (*C.A.*, 1924, **18**, 1809).
39.	B.P. 209,441.	Titanium oxide (*C.A.*, 1924, **18**, 1884).
40.	B.P. 209,480.	Titanyl sulfate (*C.A.*, 1924, **18**, 1884).
41.	B.P. 210,033.	Titanium sulfate (*C.A.*, 1924, **18**, 1884).
42.	B.P. 225,393.	Titanium pigments (*C.A.*, 1925, **19**, 1784).
43.	B.P. 227,143.	Clarifying tin and titanium solutions (*C.A.*, 1925, **19**, 2730).
44.	B.P. 228,814.	Tin. titanium, thorium and zirconium salts (*C.A.*, 1925, **19**, 3004).
45.	B.P. 247,296.	Titanium pigments (*C.A.*, 1927, **21**, 659).
46.	B.P. 256,302.	Pigments and paints (*C.A.*, 1927, **21**, 2992).
47.	B.P. 450,529.	Yeast and protein preparations (*C.A.*, 1937, **31**, 502).
48.	B.P. 478,570.	Protein containing food and medicinal preparations (*C.A.*, 1938, **32**, 5097).

49. B.P. 483,587. Food preparations (*C.A.*, 1938, **32**, 7600).
50. B.P. 489,170. Fatty acids (*C.A.*, 1939, **33**, 310).
51. U.S.P. 2,141,455. Treating yeast to obtain enzyme and vitamin products (*C.A.*, 1939, **33**, 2657).
52. B.P. 494,137. Acetone and butyl alcohol (*C.A.*, 1939, **33**, 3520).
53. French P. 834,322. Preparations from yeast or protein (*C.A.*, 1939, **33**, 3913).
54. French P. 837,651. Food products (*C.A.*, 1939, **33**, 5935).
55. French. P. 837,258. Production of acetone and butyl alcohol from molasses (*C.A.*, 1939, **33**, 7956).
55a. B.P. 509,495 Protein products (*C.A.*, 1940, **34**, 3842).
56. U.S.P. 2,206,622. Degrading protein products such as soybean meal (*C.A.*, 1940, **34**, 7640).
57. U.S.P. 2,217,264. Nutritive and therapeutic products from proteinic material (*C.A.*, 1941, **35**, 1140).
58. B.P. 516,343. Treating yeast (*C.A.*, 1941, **35**, 6058).
59. French P. 849,456. Cracking hydrocarbons (*C.A.*, 1941, **35**, 6775).
60. B.P. 529,775. Alimentary preparations (*C.A.*, 1941, **35**, 7572).
61. B.P. 537,423. Alimentary preparations (*C.A.*, 1942, **36**, 1400).
62. French P. 852,298. Acetone and butyl alcohol (*C.A.*, 1942, **36**, 2079).
63. French P. 852,540. Treating protein products (*C.A.*, 1942, **36**, 2280).
64. U.S.P. 2,136,733. Alimentary preparations from animal blood or separated blood serum (*C.A.*, 1943, **37**, 5800).
65. U.S.P. 2,329,672. Aromatic hydrocarbons from olefins (*C.A.*, 1944, **38**, 976).
66. B.P. 550,099. Ketones (*C.A.*, 1944, **38**, 977).
67. B.P. 550,174. Carboxylic acids (*C.A.*, 1944, **38**, 979.)
68. B.P. 551,215. Cracking plants and the like (*C.A.*, 1944, **38**, 3122).
69. B.P. 552,115. Aromatic hydrocarbons (*C.A.*, 1944, **38**, 3289).
70. B.P. 552,216. Aromatic hydrocarbons (*C.A.*, 1944, **38**, 3836).
71. U.S.P. 2,354,163. Lining for apparatus such as that used in the vapor phase thermal treatment of hydrocarbon materials such as oils and tars (*C.A.*, 1944, **38**, 6552).
72. U.S.P. 2,349,781. 1,2-(2',1'-Naphtho)-7,8-benzophenanthrene (*C.A.*, 1945, **39**, 1424).
73. U.S.P. 2,367,078. Selective hydrogenation of α, β-unsaturated ketones (*C.A.*, 1945, **39**, 2293).
74. U.S.P. 2,377,197. Production of acetone and butyl alcohol by fermentation (*C.A.*, 1945, **39**, 3623).
75. U.S.P. 2,386,374. Fermentation process for the production of acetone, butanol and volatile aliphatic acids (*C.A.*, 1946, **40**, 166).
76. U.S.P. 2,381,148. Dehydration of unsaturated alcohols (*C.A.*, 1946, **40**, 346).
77. U.S.P. 2,384,184. Styrene and ethylbenzene (*C.A.*, 1946, **40**, 359).
78. U.S.P. 2,388,101. Unsaturated ketones (*C.A.*, 1946, **40**, 593).
79. B.P. 564,090. Ethylene chlorhydrin (*C.A.*, 1946, **40**, 3129).
80. U.S.P. 2,397,715. Aromatics (*C.A.*, 1946, **40**, 3252).
81. B.P. 580,922. Removal of acetylene from mixtures (*C.A.*, 1947, **41**, 2066).
82. B.P. 578,082. Alkoxyisobutyric acids (*C.A.*, 1947, **41**, 2075).
83. B.P. 580,921. Synthesis of *sec.* and *tert.* ethynylcarbinols (*C.A.*, 1949, **41**, 2429).
84. B.P. 582,191. Condensations catalysed by potassium hydroxide complexes (*C.A.*, 1947, **41**, 2436).
85. U.S.P. 2,415,777. Aliphatic acids from sulphite waste liquor (*C.A.*, 1947, **41**, 2854).
86. B.P. 584,607. Conversion of alkyl α-alkoxyisobutyrates into alkyl methacrylates (*C.A.*, 1947, **41**, 3812).
87. U.S.P. 2,417,801. Bacterial fermentation (*C.A.*, 1947, **41**, 5258).
88. B.P. 575,383. Carrying out chemical processes and apparatus therefore (*C.A.*, 1947, **41**, 5295).
89. B.P. 569,373. Unsaturated ketones (*C.A.*, 1947, **41**, 5545).
90-94. B.P. 575,766; 575,768-771. Aromatic compounds (*C.A.*, 1947, **41**, 6704).
95-96. B.P. 575,636,-7. Motor fuels (*C.A.*, 1947, **41**, 6706).
97. B.P. 575,571. Treatment of olefinic hydrocarbons for the production of alcohols, ketones and other substances (*C.A.*, 1947, **41**, 6892).

98. B.P. 587,545. Mono- and disubstituted alkoxyacetic acids and α, β-unsaturated esters therefrom (*C.A.*, 1948, **42**, 591).
99. U.S.P. 2,430,416. Aromatisation of coal oil (*C.A.*, 1948, **42**, 1042).
100. B.P. 594,182. Catalyst for the addition of reactive methylene groups to the 1,4-conjugated system (*C.A.*, 1948, **42**, 2986).
101. U.S.P. 2,435,524. Acetylenic alcohols (*C.A.*, 1948, **42**, 3772).
102. B.P. 596,034. Unsaturated carboxylic acids (*C.A.*, 1948, **42**, 3774).
103. B.P. 574,085. Separation of butadiene from gaseous mixtures (*C.A.*, 1948, **46**, 6840).
104. B.P. 577,364. Dehydration of 2-methyl-3-buten-2-ol (*C.A.*, 1948, **42**, 6840).
105. B.P. 574,446. Saturated ketones (*C.A.*, 1948, **42**, 7787).
106. B.P. 574.963. Utilisation of coal oil (*C.A.*, 1949, **43**, 1951).
107. B.P. 574,977. Aromatic hydrocarbons (*C.A.*, 1949, **43**, 1955).
108. B.P. 573,527. Synthesis of *sec.* and *tert.* ethynylcarbinols (*C.A.*, 1949, **43**, 2219).
109. U.S.P. 2,456,549. Carboxylic acids (*C.A.*, 1949, **43**, 2632).
110. U.S.P. 2,456,350. Ethylene chlorhydrin (*C.A.*, 1949, **43**, 2633).
111. B.P. 573,724. Aliphatic ketones (*C.A.*, 1949, **43**, 4287).
112. B.P. 573,930. Fermentative production of a mixture of fatty acids (*C.A.*, 1949, **43**, 4810).
113. B.P. 573,216. Acetone and butyl alcohol by fermentation processes (*C.A.*, 1949, **43**, 5902).
114. U.S.P. 2,472,135. Condensation products (*C.A.*, 1949, **43**, 6664).
115. B.P. 572,643. Fermentation process (*C.A.*, 1949, **43**, 6781).
116. B.P. 572,664. Fermentation process (*C.A.*, 1949, **43**, 6781).
117. B.P. 572,642. Production of aliphatic acids by fermentation of difficultly fermentable materials (*C.A.*, 1949, **43**, 6781).
118. B.P. 572,641. Fermentation of molasses (*C.A.*, 1949, **43**, 6782).
119. B.P. 572,644. Aliphatic acids from sulphite waste liquor (*C.A.*, 1949, **43**, 6826).
120. B.P. 572,645. Ketones (*C.A.*, 1949, **43**, 7037).
121. B.P. 572,997. Separation of diolefines from gaseous mixtures (*C.A.*, 1949, **43**, 7275).
122. B.P. 572,762. Fermentation processes (*C.A.*, 1949, **43**, 7638).
123. B.P. 572,763. Fermentative production of acetone and butyl alcohol (*C.A.*, 1949, **43**,7638).
124. B.P. 572,921. Conversion of olefines into diolefines (*C.A.*, 1949, **43**, 7950).
125. U.S.P. 2,490,109. Alkoxyisobutyric acid derivatives (*C.A.*, 1950, **44**, 3012).
126. U.S.P. 2,474,175. Condensation reactions (*C.A.*, 1950, **44**, 3024).
127. U.S.P. 2,525,249. Synthesis of α-alkoxyalkanoic and alkenoic acids and esters (*C.A.*, 1951, **45**, 1621).

A CONTRIBUTION TO THE TREATMENT OF THE RELATIVISTIC KEPLERIAN MOTION

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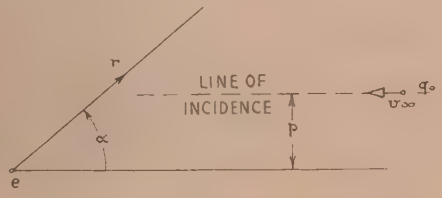
a. In his famous work on the fine structure of the spectral lines of the H-atom, Sommerfeld[1] integrated the relativistic equation of motion of an electron, which, according to the semi-classical representation of Bohr circulates round the stationary proton in a quantised orbit[1]. Sommerfeld's calculations of the "*precessing Kepler ellipses*" resulted in energy terms which agreed with observations and were therefore at that time considered as a marked proof of the (special) theory of relativity. It is known to-day that this correspondence is due, strictly speaking, to mathematical coincidence, and the rigorous treatment of the above-mentioned problem has become possible only by Dirac's four-dimensional wave mechanics. Therefore, apart from didactic purposes, no use is being made at present of Sommerfeld's results or method of approach to this problem. It is thought that this is not justified: It will be shown here, by applying his method to the classical Keplerian problem of the attraction of a body, which is moving from infinity with the initial velocity V_∞ towards the centre of attraction, that the deviations from Newtonian mechanics are *larger*, the *smaller* the ratio β_∞ of V_∞ to the speed of light c.

b. For the treatment of the problem in the field of the stationary electrical point charge $e \lesseqgtr 0$, a plane polar coordinate system, r (radial distance) and α (azimuth), is used, which is supposed to be at rest relative to a suitably chosen frame of inerta, the origin coinciding with the point charge. It is intended to find in the plane of the coordinate system the path of the electron (rest mass m_o, charge $-q_o$), which is approaching from $r \to \infty$ along a straight line antiparallel to the ray $\alpha = 0$ at a distance p in the quadrant $0 < \alpha < \pi/2$ (see Figure 1).

Figure 1



The velocity v of the electron with the coordinates (r, α) at the time t is:

$$v^2 = \dot{r}^2 + r^2\dot{\alpha}^2 \; ; \; \dot{r} = dr/dt, \; \dot{\alpha} = d\alpha/dt \tag{1}$$

and its Lagrangian function:

$$L = -m_o c^2 \sqrt{1 - (\dot{r}^2 + r^2\dot{\alpha}^2)/c^2} + q_o e/4\pi \triangle r \tag{2}$$

$\triangle$ being the so-called dielectric constant of empty space. Introducing the apparent mass of the moving electron m

$$m = m_o/\sqrt{1-\beta^2} \; ; \; \beta = v/c \tag{3}$$

into (2) the differential equations are obtained:

$$(d/dt)(m\dot{r}) - m\, r\, \dot{\alpha}^2 + q_o e/4\pi \triangle r^2 = 0 \qquad \text{and} \tag{4}$$

$$(d/dt)(m\, r^2\, \dot{\alpha}) = 0 \tag{5}$$

The Area Integral follows from (5), as

$$m\, r^2\, \dot{\alpha} = K \tag{6}$$

Received

the constant K being obtained from the kinematic boundary conditions of the controlled electron, as

$$K = m_o c p (\beta_\infty / \sqrt{1 - \beta_\infty^2}) \tag{7}$$

Writing

$$\dot{r} = \dot{\alpha} r' \; ; \; r' = dr/d\alpha \tag{8}$$

(1) gives

$$\dot{\alpha} = v/\sqrt{r'^2 + r^2} \quad = \quad c \beta/\sqrt{r'^2 + r^2} \tag{9}$$

which, substituted into (6) and with the help of (3) results in

$$\beta^2 = (K/m_o c)^2 [(r'^2 + r^2)/r^4] \Big/ \left\{ 1 + (K/m_o c)^2 [(r'^2 + r^2)/r^4] \right\} =$$

$$p^2 [(r'^2 + r^2)/r^4] [\beta_\infty^2/(1 - \beta_\infty^2)] \Big/ \left\{ 1 + p^2 [(r'^2 + r^2)/r^4] [\beta_\infty/(1 - \beta_\infty^2)] \right\} \tag{10}$$

c. In addition to the area integral there exists the *energy integral*

$$m c^2 - q_o e / 4\pi \triangle r \; = \; m_o c^2 / \sqrt{1 - \beta^2} - q_o e / 4\pi \triangle r \; = \; W \tag{11}$$

The total energy W is determined, by going to the limit $r \to \infty$, as

$$W = W_o / \sqrt{1 - \beta_\infty^2} \; ; \; W_o = m_o c^2 \tag{12}$$

Writing now (11) in the form

$$m_o^2 c^4 / (1 - \beta^2) = (W + q_o e / 4\pi \triangle r)^2 \tag{13}$$

and using (10), the differential equation of the electron path is obtained:

$$(r'^2 + r^2) / r^4 = (Kc)^{-2} (W + q_o e / 4\pi \triangle r)^2 - (m_o c/K)^2 \tag{14}$$

The unit of length, r_o is now introduced:

$$r_o = q_o e / 4\pi \triangle W_o \gtrless 0 \text{ for } e \gtrless 0 \tag{15}$$

The absolute value of $r_o = 2.8 \times 10^{-13}$ cm, in the case of $|e| = q_o$, is twice the so-called electron radius. Replacing the radial distance r by the dimensionless parameter

$$u = r_o / r \tag{16}$$

and writing

$$\gamma = r_o W_o / Kc = (r_o / p) (\sqrt{1 - \beta_\infty^2} / \beta_\infty) \tag{17}$$

(14) appears as

$$u'^2 + u^2 = \gamma^2 [(1 / \sqrt{1 - \beta_\infty^2}) + u]^2 - \gamma^2 \tag{18}$$

d. Differentiating (18) with respect to α and dividing by $2u'$ a form is obtained which is easy to integrate:

$$u'' + (1 - \gamma^2) u = \gamma^2 / \sqrt{1 - \beta_\infty^2} \tag{19}$$

Three cases have to be considered now:

1. When

$$\gamma^2 < 1 \tag{20}$$

the solution of (19) is

$$u = [\gamma^2 / (1 - \gamma^2)] [1 / \sqrt{1 - \beta_\infty^2}] + A \cos \sqrt{1 - \gamma^2} (\alpha - \alpha_o) \tag{21}$$

A and α_o being two constants. Substituting the expression for u into (18), the condition is obtained that

$$A^2 (1 - \gamma^2) = [\gamma^2 / (1 - \gamma^2)] [1 / (1 - \beta_\infty^2)] [\gamma^2 + (1 - \gamma^2) \beta_\infty^2] \tag{22}$$

Substituting this expression for A into (21) and using the relation (16) the *equation of the electron path* is obtained:

$$r/r_o = [(1-\gamma^2)/\gamma^2]\sqrt{1-\beta_\infty{}^2}[1/(1-\sqrt{1+[(1-\gamma^2)\beta_\infty{}^2/\gamma^2)}]\cos\sqrt{1-\gamma^2}(\alpha-\alpha_o) \quad (23)$$

The value of the constant of integration α_o follows from the direction of approach $\alpha = 0$, as required above

$$\alpha_o = \arccos[\gamma / \sqrt{\gamma^2 + (1-\gamma^2)\beta_\infty{}^2}] \quad (24)$$

Two cases should be discussed now:

a′: The approaching electron is repulsed by a stationary *negative* point charge at the origin. Then, according to definition (15), $r_o < 0$, and $0 < \alpha_o < \pi/2$ and $0 \leq \alpha \leq 2\alpha_o$ is to be chosen.

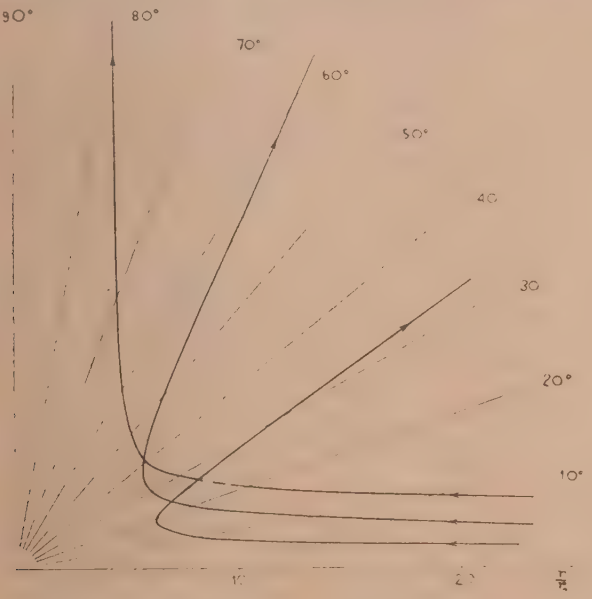


Figure 2 $[\beta_\infty = 0.5]$

The *electron paths* are *hyperbola-like trajectories* (see Figure 2), which approach the origin at the azimuth $a = a_o$ to the smallest distance

$$r_{\min} = (-r_o)(\sqrt{1-\beta_\infty{}^2}/\beta_\infty{}^2)\{1+\sqrt{1+[(1-\gamma^2)\beta^2{}_\infty/\gamma^2]}\} \quad (25)$$

b′: The approaching electron is attracted by a stationary *positive* point charge at the origin. Then, according to (15), $r_o > 0$ and $(-\pi/2) < \alpha < 0$ and $(-\alpha_o) \leq \alpha \leq 2\pi-(-\alpha_o)$.

It can be seen in Figure 3 that in this case hyperbola-like trajectories result only if γ is sufficiently small, while for γ >1 the trajectories are loop shaped. These can be considered as the analogue to the *precessing elliptical orbits* of the Bohr-Sommerfeld atom model mentioned in the introduction.

2. On the other hand, if, in contradistinction to (20)

$$\gamma^2 > 1 \quad (26)$$

(23) changes into

$$r/r_o = [(1-\gamma^2)/\gamma^2]\sqrt{1-\beta_\infty{}^2}\{1/[1-\sqrt{1-(\gamma^2-1)\beta_\infty{}^2/\gamma^2}\cosh\sqrt{\gamma^2-1}(\alpha-\alpha_o)]\} \quad (27)$$

Two cases of different character occur again:

a″: Assuming $e < 0$ (repulsion), the electron trajectories are hyperbola-like for $\gamma^2 > 1$, just as in the case of $\gamma^2 < 1$ (see Figure 2).

b″: In the case of $e > 0$ (attraction) the electron paths are spirals winding closer and closer round the origin (see Figure 3) and consequently the electron collides with the positive ion.

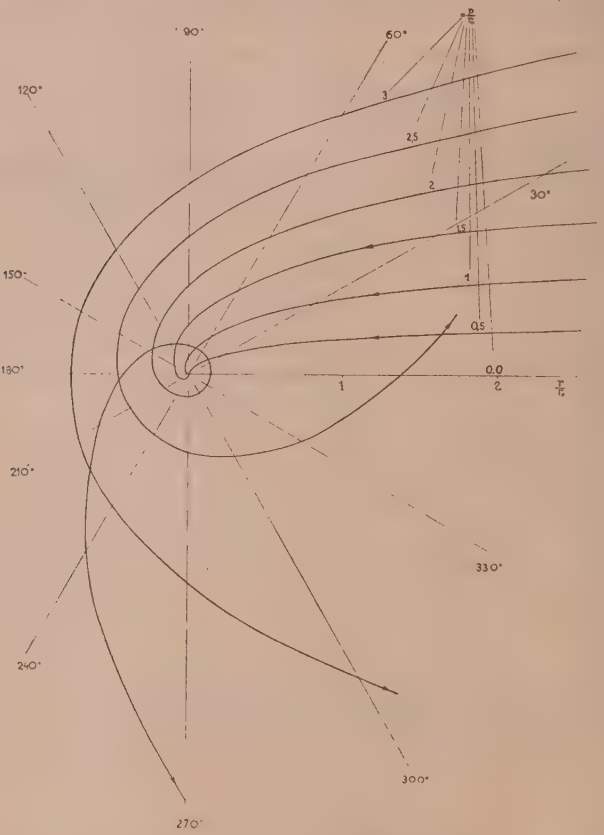


Figure 3
[$\beta_\infty = 0.5$]

3. In the case

$$\gamma^2 = 1 \tag{28}$$

(23) and (27) are not applicable; but taking $\gamma \to 1$, the common limiting values are:

$$r/r_o = -2\sqrt{1-\beta_\infty^2}/\alpha\,(2\beta_\infty - \alpha)\ ;\ e < o \tag{29}$$

$$r/r_o = 2\sqrt{1-\beta_\infty^2}/\alpha\,(2\beta_\infty + \alpha)\ ;\ e > o \tag{30}$$

The curve representing (29) is a *hyperbola-like trajectory*, while that representing (30) is a spiral winding round the origin.

e. The basic problem of this presentation can be discussed now: How do the results of the relativistic theory compare with those of Newtonian Mechanics?

1. Considering definition (17) again, it is found by going in the mathematically formal way to infinite speed of light

$$\lim_{c\to\infty} \gamma = 1 \lim_{c\to\infty} (q_o e / 4\pi \triangle p)(\sqrt{1-(v_\infty/c)^2}/m_o c v_\infty) = o \tag{51}$$

and

$$\lim_{c\to\infty} \beta_\infty/\gamma = 1 \lim_{c\to\infty} v_\infty/c\gamma = (4\pi \triangle p/q_o e) m_o v_\infty^2 \tag{32}$$

Also, from (24): $\lim_{c\to\infty} \alpha_o = \arccos\,[1/\sqrt{1+[(4\pi \triangle p/q_o e)\, m_o v_\infty^2]^2}$ (33)

and (23) is transformed by making use of (15) into

$$\lim_{c\to\infty} r/p = (4\pi \triangle p/q_o e)\, m_o v_\infty^2 \Big/ \left\{1 - \sqrt{1+[(4\pi \triangle p/q_o e)\, m_o v_\infty^2]^2}\cos(\alpha - \alpha_o)\right\} \tag{34}$$

which is identical with the Newtonian Kinematics of this problem.

2. It might be supposed, that going to the limit $v_\infty \to 0$ for constant c would also lead to Newtonian Mechanics. This assumption is, however, correct only for the dynamic behaviour of a pair of charges of the same polarity. The relativistic kinematics of the attraction of charges of opposite polarity differs from the Newtonian laws of the Keplerian motion, the more so, the smaller β_∞.

The proof of this seemingly paradoxical statement follows from the definition of γ (17). For the present case, it is found by series development, in contradistinction to (31), that

$$1/\gamma = (4\pi \triangle p/q_o e)\,(m_o c^2 \beta_\infty / \sqrt{1-\beta_\infty^2}) = (4\pi \triangle p/q_o e)\, m_o c^2 \beta_\infty + \dots \tag{35}$$

Further, it follows from:

$$\cosh \sqrt{\gamma^2-1}\,\alpha_o = 1/\sqrt{1-[(\gamma^2-1)/\gamma^2]\,\beta_\infty^2} = 1 + (1/2)\,\beta_\infty^2 + \dots \tag{36}$$

that:

$$\alpha_o = \pm (\beta_\infty/\gamma + \dots) = \pm [(4\pi \triangle p/q_o e)\, m_o c^2 \beta_\infty^2 + \dots] \tag{37}$$

For the case of repulsion ($e < 0$, $\alpha_o > 0$) it is seen from (20) that the smallest distance of the approaching electron from the origin is obtained from

$$r_{\min}/r_o = [(1-\gamma^2)/\gamma^2]\sqrt{1-\beta_\infty^2}\,[1/(1-\sqrt{1-[(\gamma^2-1)/\gamma^2]\,\beta_\infty^2})] = -2/\beta_\infty^2 + \dots \tag{38}$$

as

$$r_{\min} = -(q_o e/4\pi\triangle)(2/m_o v_\infty^2) \tag{39}$$

The same expression is obtained for $\alpha = \alpha_o$ from (34), when

$$r_{\min} = -p\left[(4\pi\triangle p/q_o e)\, m_o v_\infty^2\right] \Big/ \left[1-\{1+1/2\,(4\pi\triangle p/q_o e)\, m_o v_\infty^2 + \dots\}\right]$$
$$= -(q_o e/4\pi\triangle)(2/m_o v_\infty^2) + \dots \tag{40}$$

In the case of attraction, however, ($e > 0$, $\alpha_o < 0$) the relation (27) reduces, with the help of (36), to

$$r/r_o = 1/\left[\cosh\{(q_o e/4\pi\triangle p)(\alpha/m_o c^2 \beta_\infty^2)\} - 1\right] + \dots \tag{41}$$

Instead of a classical Keplerian hyperbola, along which the electron approaches the attraction center to a minimum distance and then travels to infinity, a spiral trajectory results leading to collision of the interacting particles. This *capture effect* might be visualized, if, with respect to the electron, an *effective radius* R is ascribed to the stationary positive ion at the origin.

This radius is the critical approach distance $p = p_{kr}$, which is the limiting value of this parameter of the trajectory for $\gamma \to 1$. It follows from (17) in connection with (3) and (25) that

$$R = r_o \sqrt{1-\beta_\infty^2}/\beta_\infty = (q_o e/4\pi\triangle)(1/m v_\infty c) \tag{42}$$

The expression

$$\lambda = h/mv_\infty \tag{43}$$

gives the de Broglie wavelength of the approaching electron, where h is Planck's quantum of action. Thus the relation

$$R/\lambda = q_o e/4\pi\triangle hc \tag{44}$$

is obtained from (42). The right hand side of this relation is, for $e = q_o$, exactly $1/2\pi$-times the *fine structure constant* of Sommerfeld:

$$q_o^2/4\pi\triangle hc = 1.16\cdot10^{-3} = (1/2\pi)(1/137) \tag{45}$$

A "slow" electron emitted from a hot cathode at the absolute temperature $T^{o}_{K} = 2000^{o}\ K$ moves with a statistical average speed of

$$v = \sqrt{3kT_K/m_o} = \sqrt{3\,[(1.381\cdot10^{-23}\cdot3000)/9\cdot10^{-35}]} = 3.72\cdot10^{7}\ \text{cm/sec} \qquad (46)$$

Taking this to be the speed of approach v_{∞}, the de Broglie wavelength of this electron is found to be

$$\lambda = 6.632\cdot10^{-34} / (9\cdot10^{-35})\ (3.72\cdot10^{7})\ \text{cm} = 19.7\cdot10^{-8}\text{cm} \qquad (47)$$

Using the values from (45) and (47) the effective radius of the positive ions is evaluated as

$$R = (1.16\cdot10^{-3})\ (19.7\cdot10^{-8})\ \text{cm} = 228\cdot10^{-12}\text{cm} \qquad (48)$$

This is about 1500 times larger than the radius of the electron.

It follows thus from this relativistic treatment that Rutherford's theory of the scattering of α-particles by atomic nuclei remains valid. On the other hand the classical theory of the recombination of ions of opposite charges in the plasma of electrical discharges should require a fundamental revision.

f. If the interacting particles can move about freely, the assumption of a charge at rest at the origin offers a useful approximation for the behaviour of the system only if the apparent mass of the approaching electron is small compared with that of the other particle. This condition can be maintained in the case of repulsion by the choice of a sufficiently large rest mass, for the ion at the origin. In the case of attraction and spiral trajectory, however, the apparent mass of the electron increases constantly while it approaches the positive ion. The rigorous treatment of this process leads therefore to that of a relativistic two-body problem, the exact solution of which is not known. Further account should be taken of the electro-magnetic radiation of the accelerated electron for a more accurate analysis of the investigated problem.

REFERENCE

1. SOMMERFELD, A., 1922, *Atombau und Spektrallinien*, 3 ed., Braunschweig, Vieweg, p. 570 and 732.

THE DIELECTRIC CONSTANT OF 'FREE' AND 'BOUND' WATER AT MICROWAVE FREQUENCIES

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INTRODUCTION

The study of water in its various chemical combinations with other molecules is of great importance in the fields of crystallography, chemistry, and biology. It has been suggested by Freymann[1,2] that dielectric dispersion of water in the microwave region may serve to differentiate between water held in crystals and adsorbed water. Preliminary results of dielectric measurements at 3 cm on crystalline water in $CuSO_4 \cdot 5HO_2$ and $CaCl_2 \cdot 2H_2O$ [3], and the role of water in aqueous thixotropic gels[4] have been reported by us. In the meantime additional information on this subject has been accumulated both in this laboratory and by the French group under Prof. Freymann. It is the purpose of this article to assess and summarize some of the results obtained.

DIELECTRIC DISPERSION OF WATER

During the last few years a number of authors[5,6,7,8] have reported measurements of the dielectric properties of water in the region from 0.6 cm to 10 cm over a wide range of temperature and using various techniques. The results, using data of Lane and Saxton and of Cook are presented in Figure 1. These results can be analyzed in terms of Debye's expression for the radio dispersion of the dielectric constant of a polar liquid in a time dependent field[9].

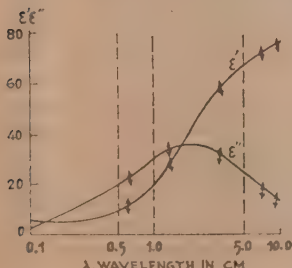

Figure 1
Dielectric constants of water at 20°C (based on Lane & Saxton, Cook's). Arrows experimental points, curve derived from equations 1,2.

These relations are given by

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) / [1 + (\omega\tau)^2] \quad (1)$$

$$\varepsilon'' = (\varepsilon_s - \varepsilon_\infty) / [1 + (\omega\tau)^2] \quad (2)$$

$$\varepsilon''/\varepsilon' = \tan\Theta \quad (3)$$

where $\varepsilon = \varepsilon' - i\varepsilon''$ is the complex dielectric constant, $\tan\Theta$ the dissipation factor, ε_s the static dielectric constant (the dielectric constant on the low frequency side of the dispersion region), ε_∞ that corresponding to the high frequency side, ω the angular frequency and τ the relaxation time.

Debye assumed that the molecular dipoles, pictured as spheres, rotate in a viscous fluid opposed by a retarding force given by Stokes's law. From this he deduced an espression for the relaxation time as

$$\tau = 4\pi\eta a^3 / kT \quad (4)$$

where η is the macroscopic viscosity at an absolute temperature T and a is the molecular radius. According to this simple picture, the relaxation time is proportional to the molecular volume, and, therefore, large molecules will show dispersion in the Mc. range and smaller molecules in the microwave region.

A more modern approach assumes that the molecule can take two or more equilibrium positions, separated by potential energy barriers. The relaxation time is now regarded to be a measure of the transition probability. It can be shown[10] that such a view leads also to the same dispersion relations (1) and (2).

* The untimely death of Mr. Joseph Baruch, just as he was about to present this work as part of his Doctorate, was a severe blow to his friends and colleagues and ended a promising career in physics.

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These relations can be generalized to include distribution of relaxation times due to many potential barriers of various height. In this case the dispersion curve as given by (2) becomes appreciably broader.

The dielectric measurements on water show that the results fit very closely to Debye's theory of dispersion (see Figure 1), and indicate one relaxation time or a very narrow range of relaxation times[7,8]. From these data one obtains a best fit for $\varepsilon_\infty = 5.0 \pm 0.5$.

Any structural theory of water has to explain not only the high static dielectric constant (about 80), but also the variation of the dielectric constant and dissipation factor with temperature and frequency. The above curves point to very simple properties of the water molecule.

There are several theories on the structure of water and ice[11]. Bernal and Fowler[12], in a classical paper, describe water as a broken down ice structure. The four nearest neighbours of a given molecule form a regular tetrahedron by means of hydrogen bonds. The structure is continuously breaking and reforming. A calculation of the static dielectric constant according to Kirkwood's theory of liquids[13,14] leads to the right order of magnitude and temperature dependence. Lennard-Jones and Pople[15] consider a model in which considerable bending and distortion of bonds occur. They also obtain fair agreement of the temperature variation of ε_s. The absolute calculated value of the dielectric constant, however, is somewhat low.

The complexity of the structure of water and its properties of association are difficult to reconcile with the apparent single relaxation time. Haggis et al.[16] using a statistical, semiquantitaitve approach, based on the model of Bernal, have treated water as existing in 5 states; 4-bonded, 3-bonded, 2-bonded, 1-bonded and zero bonded. These bonds are in a state of being broken and reformed constantly. The authors assume that the dispersion curve in the microwave region is essentially due to 4- and 3-bonded molecules which cannot rotate without breaking bonds*.

The two, one, and zero bonded molecules can rotate and should show dispersion in the infra red and far infra red region. In the far infra red region there is some indication of such a dispersion. Saxton[7], however, explains this as due to Frohlich's resonance absorption[17]. The possibility of a distribution of relaxation times should not be dismissed a priori. Further experimental work in the far infra red region, in particular the temperature dependence of the dielectric constant, may indicate which interpretation is correct.

Some light may be thrown on the structure of water by microwave measurements on its dielectric behaviour in crystals, gels, and other chemical associations. If the water molecule is unable to rotate, or if the molecules form stronger bonds to the solute than to the surrounding water molecules, we should expect no dispersion in the microwave region. We shall describe water which shows dispersion in the microwave regon as rotationally "free" and that which does not as "bound"[18]. Measurements of this kind will not only give some indication of the interaction of the water molecule with other molecules, but will also give some information on the structure of substances like gels and hydrates.

CRYSTALLINE WATER

We have tested on powdered $CuSO_4 \cdot 5H_2O$ [3] Freymann's suggestion that one may differentiate between crystalline and adsorbed water by microwave dielectric measurements. The dissipation factor of 0.002 for copper sulphate is so small as to preclude the possibility of dispersion of water molecules. An analysis of the crystal structure[19] and investigations of its paramagnetic resonance[20] indicate tetragonal symmetry. The four water molecules are almost equidistant from the copper ion with the oxygen atoms oriented towards the copper. The fifth water molecule is in between these units. Copper sulphate loses four water molecules at 110°C and the fifth at 150°C. We have measured the dielectric constant at 3 cm in the range from $-70°$ to 150°C. and found sharp, irreversible increases in the dielectric constant and dissipation factor at those two temperatures. If the sample is cooled again to room temperature, then after some hours values close to the original dielectric constant are obtained. Apparently the water molecules are readsorbed and later tightly bound as crystalline water. An anomaly was found in the region from 92° to 99°C. Here the dissipaton factor increases sharply and is reversible with the temperature without any time lag. The reversible reaction excludes the possibility that water molecules are set free. It is possible that in this temperature range there occurs a order-disorder transition[10,29].

* Haggis et al. find experimentally that dissolved electrolytes shorten the relaxation time and dissolved organic substances lengthen it. They infer from this that the addition of ions causes an increase in the percentage of bonds broken, whereas hydrogen bond forming groups like organic solutes cause a decrease in the number of bonds broken.

Another possibility is that water molecules are released from the crystal structure and diffuse to the grain boundaries where they are held as adsorbed water. Further investigation under vacuum conditions would be interesting.

HYGROSCOPIC SALTS

We have investigated the dielectric properties of $CaCl_2$ and NaCl as a function of the percentage of adsorbed water. A standing wave method with a shortcircuited waveguide was employed[21,22]. The absorption cell consisted of a waveguide, the two narrow sides of which had been replaced by a close wire mesh. The amount of water adsorbed was measured as an increase in the weight of cell and sample. The sample was exposed for fixed intervals to a stream of air saturated with water vapour which was sucked through the sample through the wire mesh. At the end of the interval the dielectric constant was measured until equilibrium had been established. In all cases the dissipation factor fell from a high value, characteristic of 'free' water, to a value lower than 0.01. The speed of this reaction depended on the amount of water already bound to the salt. The velocity of the reaction was very fast in the case of $CaCl_2$—of the order of seconds—and slow in the case of NaCl and $CuSO_4$—of the order of tens of minutes. We suggest that the reaction is one from adsorbed water to crystalline water. Similar results were found by Freymann[23] for NaCl and by Rohmer[24] for Na_2SO_4. The latter crystal is able to absorb ten water molecules. After exposing for several days the salt to a humid atmosphere Rohmer found that the salt had adsorbed 5 water molecules and started to show a small loss factor. This loss factor increases with the increase of water uptake until the limit of 10 H_2O. According to our interpretation this salt absorbs water very slowly and the reaction proceeds slower the greater amount of crystalline water already present, and in particular very slowly as the concentration approaches the limit of 10 molecules. The reaction is very temperature dependent, since with an increase of temperature the salt-water bonds become weaker.

Le Bot and Le Montagner[25] as well as Freymann[26] have investigated in detail the behaviour of the dielectric constant of silica gel as a function of frequency and temperature. They find one dispersion region at 17,000 Mc and one lower than 1000 Mc. The dispersion at 17,000 Mc persists even after heating the silica gel to 110°C and driving off 18% of the water (silica gel of 28% water loses 18% at 110 and 10% at 600°C.). They assume from these results that associated water has a dispersion region in the cm range and unassociated water at lower frequencies. Rolland and Bernard[27], working in the kc range, far removed from the dispersion range of water, report two dispersion regions one roughly 0°C and one at −90°C which they also assume to be due to associated and unassociated water respectively[28]. This view is contrary to the views on the structure of water by Haggis et al. Moreover, the unassociated water should show dispersion at higher frequencies rather than at lower. It is possible that the dispersion found by Le Bot at lower frequencies may be due to rotating phases[29] or order-disorder transition. It is interesting to note in this connection that Bayley[30] had found similar peaks in the dissipation factor for presumably adsorbed water in inorganic molecules in the audio frequency range. The low frequency and the sharpness of the peaks seem to exclude a Debye relaxation mechanism. Our work on gelatin, moreover, indicates that the dispersion in the microwave region is not due to bound water.

AQUEOUS GELS AND THIXOTROPIC GELS

The problem of the role of water in the formation of gels has occupied our attention for some time[4]. The structure of gels is not completely understood. We have investigated the temperature dependence of the dielectric constant of gelatine at 3 cm of a 15% gelatin gel.* Figure 2 shows the results. Similar resuilts were obtained for other concentrations. Gelatin sets into a gel around 35°C. As seen from the graph the variation of the dielectric constant with temperature shows no discontinuity in this region.

Aqueous thixotropic gels, like alumina molybdate, showed no change of dielectric constant during the transition from sol to gel. The dielectric constant and dissipation factor are close to that of water.

Our results indicate that the gel structure is mainly due to the solute particles which apparently form linkages through the gel. A theory of such a structure called 'random mesh' or 'cardhouse' structure has been proposed for thixotropic gels[31]. In such a structure the water molecules would be free to

* The authors gratefully acknowledge the help of Dr. H. Mayer of the Dept. of Biochemistry in the analysis of the percentage of gelatin.

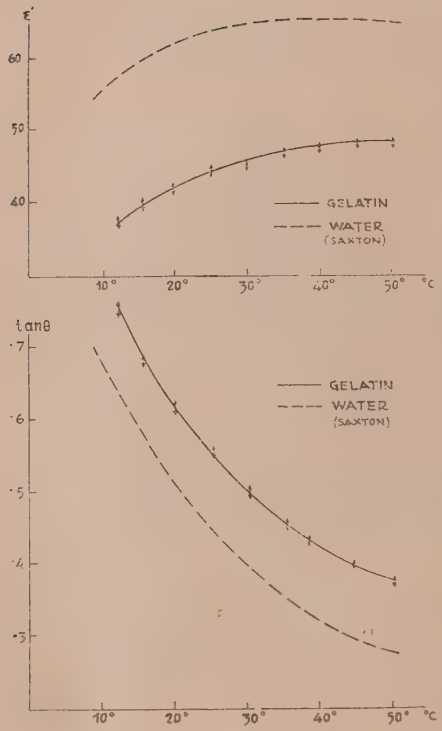

Figure 2
Dielectric constants and dissipation factor tan Θ of gelatin as function of temperature

rotate even in the gel state within the open meshes. One can possibly attribute the peaks observed by Le Bot and Le Montagner on silica gel to the water free to rotate in the high frequency field. The relative height of the observed maxima of 28% and dehydrated, 10% silica gel is approximately the ratio of the two percentages of the absorbed water.

ESTIMATION OF HYDRATION

There is no theory, at present which gives the dielectric constant of a mixture in a high frequency field. The usual procedure in the interpretation of the results is to calculate the static dielectric constant by means of equation(1) and (2) and to compare with any existing theory[32,33,34,35,36] on the static dielectric constant of a mixture. It is found that these two values agree more or less, except in the case of hydrated organic molecules. Haggis et al.[16] have sugested that this may be due to the bound water of hydration. The estimation depends on the fact that, in the high frequency field, the large organic molecules, and especially those with bound water, contribute to the dielectric constant only by virtue of their atomic and electronic polarization. Fricke's theory of mixtures[35], for example, leads to the simple expression for the dielectric constant of a mixture

$$\varepsilon = \varepsilon_{\text{water}} + [\beta\varrho / (1 - \varrho)] (\varepsilon_{\text{solute}} - \varepsilon) \qquad (5)$$

neglecting $\varepsilon_{\text{solute}} / \varepsilon_{\text{water}}$

For low concentrations one may write

$$\varepsilon = \varepsilon_{\text{water}} - \beta\varrho (\varepsilon_{\text{water}} - \varepsilon_{\text{solute}}) \qquad (6)$$

where ϱ is the volume fraction of the solute, β a parameter calculated by Fricke for different axial ratios and given in Table I. For small concentrations the static dielectric constant ε_s of the mixture depends nearly linearly on the concentration c of the solute and one may write

TABLE I

Shape	β
spheres	1.5
prolate spheroids axial ratio 5:1	1.62
long needles	1.67
oblate spheroids, axial ratio 1:5	2.2
oblate spheroids, axial ratio 1:10	3.0

$$\left.\begin{aligned} \varepsilon &= \varepsilon_{\text{water}} - \delta c \\ \delta &= \beta [(\varepsilon_{\text{water}} - \varepsilon_{\infty\,\text{solute}}) v + (\varepsilon_{\text{water}} - \varepsilon_{\infty\,\text{water}}) \omega] / 100 \end{aligned}\right\} \qquad (7)$$

where v is the partial specific volume in g per 100 m and $\varepsilon_{\infty\,\text{water}}$, $\varepsilon_{\infty\,\text{solute}}$ the high frequency dielectric constant of the water and solute respectively. From the decrement δ the bound water fraction ω can be found as a function of the axial ratio. Buchanan et al.[37] using this theory find that proteins can be described by one single relaxation time. Using values $\varepsilon_{\infty\,\text{water}} = 5.5$, $v = 0.75$, $\varepsilon_{\infty\,\text{solute}} = 2$ they calculate ω the hydration between 0.1 and 0.2 g of water per g. of protein. They also find that the amount of bound waterfor serum albumin is constant over the temperature range 15°C to 40°C.

We have calculated the hydration of gelatin using values $\varepsilon_{\infty\,\text{water}} = 5.0$, $v = 0.75$, and $\varepsilon_{\infty\,\text{solute}} = 3.55$. Experiments in this laboratory on dry gelatin and yeast have shown that the dielectric constant in the

microwave region is higher than the square of the refractive index (2). For these powdered materials we have obtained $\varepsilon = 2.1$. Using reasonable values for the partial volumes and shape factor, we obtain $\varepsilon = 3.4$—3.8 for the bulk dielectric constant. Some evidence that proteins have such a high dielectric constant has been given by Laird[38], working on dried keratin ($\varepsilon = 3.6$) and by Shaw and Windle[39] on wool fibres ($\varepsilon = 3.54$).

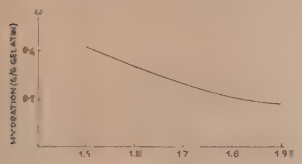

Figure 3
Hydration as a function of the form factor β

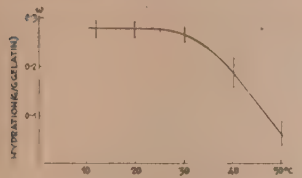

Figure 4
Hydration as a function of temperature, assuming 1.7 and to be constant over the temperature range

The structure of gelatin in the gel state is not known. We have, therefore, calculated the hydration at 20°C for various form factors β. This is shown in Figure 3. Figure 4 gives the variation of hydration of gelatin with temperature, assuming arbitrarily a form factor of 1.7. As seen from this graph the curve is approximately linear till 30°C and then falls off sharply. This can be interpreted that the hydration in the sol state is much less than in the gel state. We are inclined to think, however, as indicated in the discussion on gels, that the structure of the solute changes very rapidly during the transition from sol to gel. The sudden change of slope, just at the range of temperature when this sol-gel transition occurs, seems to give additional support to this interpretation. A small change of hydration with temperature cannot be ruled out, however.

The accuracy of this method of estimation of hydration cannot be better than any of the theories on the dielectric constant of a mixture. For any given structual parameter β the accuracy of the derived hydration is probably better than 70%. (This includes the uncertainty of the validity of the various theories as well as experimental errors.) This is about as good as any of the usual methods of estimation of hydration in chemistry. The accuracy of estimating the change of hydration with temperature, assuming any given theory on mixtures and a constant shape factor (as in proteins), is better than 25%.

We have also measured the dielectric constant of commercial yeast. Figure 5 and Figure 6 show the dielectric constant and loss factor of yeast as a function of the percentage of water content (g of water

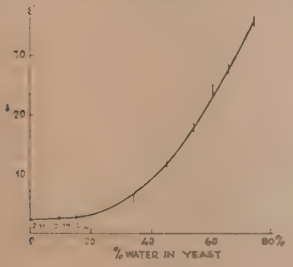

Figure 5
Dielectric constant of yeast as a function of water content

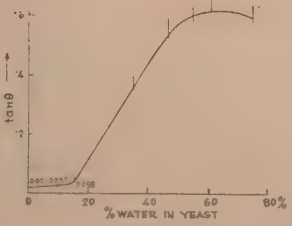

Figure 6
Dielectric loss factor of yeast as a function of water content

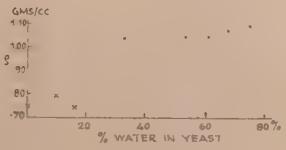

Figure 7
Density in g/cc for yeast

per 100 g of yeast). Figure 7 gives the corresponding density of the yeast in its various stages of dehydration. The experimental difficulties of obtaining homogeneous, partially hydrated samples were great. The samples were dried at 37°C. for various lengths of time .The last traces of water for completely dehydrated yeast were removed after prolonged heating at 100°C and higher, Many of the points indicated in Figures 5 and 6 are a statistical average of several experiments for the same stage of dehydration and nearly the same density. The temperature of the yeast at the at the time of measurement was between 21—23°C.

From these given data it is difficult to estimate the hydration by the method outlined in the previous paragraphs. In the case of yeast both the partial volume and the shape of the molecule are unknown. Moreover, since we have measured only at one wavelength, we are not sure whether the dielectric constant follows a Debye relaxation curve. Nevertheless, the shape of these curves may permit a simple

estimate of the hydration. If we interpret the nearly horizontal initial section of Figures 5 and 6 as being due to bound water, this would indicate a value of 10—15%, or between 0.11 to 0.18 g of water per g of dry yeast. This is in agreement with the values obtained by Buchanan et al. for various proteins. It should be emphasized here that the values of hydration both for gelatin and yeast are considerably lower than those obtained by convential methods. On the other hand, the definition of hydration as given here, as irrotationally bound water, is not identical with that generally used in chemistry and biology.

APPLICATIONS

The differences of the properties of "free" and "bound" water are important in many branches of science. In biology, for example, one would like to investigate the amount of bound water in spores and other living matter. Dr. E. Alexander, of the Department of Physics, has suggested an investigation of the dielectric properties of wool fibres under various conditions of hydration. The role of bound water is also of great importance to soil science.

ACKNOWLEDGEMENTS

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REFERENCES

1. Freymann, M. and Freymann, R., 1951, *Compt. Rend.*, **232**, 401.
2. Freymann, R., 1950, *Physica*, **17**, 331.
3. Baruch, J. and Low, W., 1953, *Bull. Res. Counc. of Israel*, **2**, 429.
4. Low, W. and Baruch, J., 1952, *Bull. Res. Counc. of Israel*, **2**, 272.
5. Collie, C. H., Hasted, J. B. and Ritson, D. M., 1948, *Proc. Phys. Soc.*, **60**, 145.
6. Lane, A. and Saxton, J. A., 1952, *Proc. Roy. Soc.*, **A213**, 400.
7. Saxton, J. A., 1952, *Proc. Roy. Soc.*, **A213**, 475.
8. Cook, H. F., 1952, *Brit. J. Appl. Phys.*, **3**, 249.
9. Debye, P., 1945, *Polar Molecules*, Dover Publications, New York.
10. Frohlich, H., 1949, *Theory of Dielectrics*, The Clarendon Press, Oxford.
11. Campbell, E. S., 1952, *J. Chem. Phys.*, **20**, 1411.
12. Bernal, J. D. and Fowler, R. H., 1933, *J. Chem. Phys.*, **1**, 515.
13. Kirkwood, J., 1939, *J. Chem. Phys.*, 7, 911.
14. Oster, G. and Kirkwood, J. G., 1943, *J. Chem. Phys.*, **11**, 175.
15. Lennard-Jones, F. R. S. and Pople, J. A., 1951, *Roy. Soc.* **A205**, 155.
16. Haggis, G. H., Hasted, J. B. and Buchanan, J. T., 1952, *J. Chem. Phys.* **20**, 1452.
17. See reference 10, page 98.
18. This follows from a suggestion by Girard and Abadie, 1946, *Trans. Far. Soc.*, **42A**, 47.
19. Wykoff, R. W. G., 1948, *Crystal Structures*, Interscience Publishers, N.Y.
20. Kikuchi, C. and Spence, R. D., 1950, *Amer. J. Phys.*, **18**, 167.
21. Roberts, S. and von Hippel, A. R., 1946, *J. Appl. Phys.*, **17**, 610; *ibid*, 1947, *J. Appl. Phys.*, **18**, 789.
22. Baruch, J. and Low, W., 1953, *Bull. Res. Counc. of Israel*, **2**, 430.
23. Freymann, R. and Rohmer, R., 1951, *Compt. Rend.*, **233**, 957.
24. Rohmer, R., 1951, *Compt. Rend.*, **233**, 864.
25. Le Bot, J. and Le Montagner, S., 1951, *Compt. Rend.*, **233**, 862.
26. Freymann, M. and Freymann, R., 1951, *Compt. Rend.*, **233**, 1096.
27. Rolland, M. Th. and Bernard, R., 1951, *Compt. Rend.*, **233**, 1098.
28. Girard and Abadie (ref. 18) working on gluten interpret their results the same way.
29. Hoffmann, J. D. and Smith, A. P., 1950, *J. Amer. Chem. Soc.*, **72**, 171.
30. Bayley, S. T., 1951, *Trans. Far. Soc.*, **47**, 519.
31. Goodeve, C. F., 1939, *Trans. Far. Soc.*, **35**, 343.
32. Bruggemann, D. A. G., 1935, *Ann. Phys.*, **24**, 636.
33. Bottcher, J. C. F., 1945, *Rec. Trav. Chim.*, **64**, 47.
34. Ollendorf, F., 1931, *Arch. f. Electrotechnik*, **25**, 436.
35. Fricke, H., 1924, *Phys. Rev.*, **24**, 575.
36. Polder, D. and van Santen, J. H., 1946, *Physica*, **17**, 257.
37. Buchanan, J. D., Haggis, G. H., Hasted, J. B. and Robinson, P., 1952, *Proc. Roy. Soc.*, **A213**, 379.
38. Laird, E. R., 1952, *Can. J. Phys.*, **30**, 683.
39. Shaw, T. M. and Windle, J. J., 1953, *Bull. Amer. Phys. Soc. North Car. meeting March* 1953.

GEIGER-COUNTER MEASUREMENTS OF SINGLE-CRYSTAL BRAGG REFLECTIONS. THE GEOMETRICAL PROBLEM

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INTRODUCTION

Recent advances in the design of Geiger-Müller tubes for the detection of x-ray quanta, together with the recognition of the advantages offered by Geiger counters over the photographic film for the measurement of x-ray intensities, have led to the increasing use of such counters in crystallographic investigations. However, while the Geiger counter has been extensively employed in the analysis of spectra from powdered specimens, its use in the measurement of the Bragg reflections from single crystals has been very limited, although it is in this field that the counter may be expected to influence profoundly the future development of structure analysis. Thus Cochran[1] has shown that the increase in accuracy of the observed structure factors can lead to a more accurate determination of bond lengths, to a more complete knowledge of the thermal vibrations of the molecule, and possibly to a more detailed description of the electron-density distribution within the molecule. We believe, furthermore, that this gain in accuracy, aided by low-temperature measurements, will yield better-defined vector maps and so enhance the value of the Patterson method in the early stages of structure analysis. That counters have nevertheless found but scant use as yet in single-crystal work may well be due to the lack of a spectrometer for the convenient and systematic measurement of the Bragg reflections. It is the purpose of this paper to discuss the fundamental problems involved in the use of a Geiger counter for the measurement of the integrated Bragg reflections from a single crystal and to propose a number of methods whereby this may be achieved. We do not here consider any mechanical or constructional details, which belong properly to the sphere of the instrument designer.

The principal requirements of a satisfactory procedure may be outlined as follows:

1. It must provide for the recording of the maximum number of Bragg reflections obtainable with any given wave length.
2. A minimum of computation should be required for the proper orientation of the crystal and of the counter tube.
3. The motions required should permit the maximum simplicity in both design and operation.

STATEMENT OF PROBLEM

A disadvantage of the Geiger counter, or of any other electronic counter, is that, unlike the photographic film, it can measure only one intensity at a time. In order that the Bragg spectra produced by a crystal may be individually recorded, they must be presented to the counter through a limiting aperture, which prevents more than one reflection from entering the effective volume of the counter during each counting period. For each reflection, therefore, provision must be made, not only for the correct orientation of the crystal in the primary x-ray beam, but also for the alignment of the counter cylinder in the direction of the reflected beam. Because the counter sensitivity depends, in general, on the path of the radiation inside the counter tube, it is necessary to preserve the identical orientation of the counter with respect to each reflected beam that is to be measured. It is also desirable, in order that errors due to air scattering may be avoided, that the crystal-to-counter distance, as well as the target-to-crystal distance, be constant for all reflections. The locus of the Geiger-Müller tube should accordingly lie on a sphere centered at the crystal, the cylinder axis being directed at all times towards the crystal.

The geometric conditions governing the Bragg reflections from a single crystal in a collimated beam of monochromatic x-rays are most conveniently discussed by reference to the reciprocal lattice and the sphere of reflection. We may, following Buerger[2], whose notation we shall adapt to our needs as far as practicable, imagine the reciprocal lattice drawn to such a scale that the sphere of reflection has unit radius. The problem of successively generating the various Bragg spectra is equivalent to the prob-

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lem of rotating the reciprocal lattice about its origin so as to bring each of the reciprocal-lattice points in turn onto the sphere of reflection. For each such reflection to be properly recorded, the detector must be placed along the line of the radius SP, where S is the centre of the sphere of reflection and P the position, on the sphere of reflection, of the corresponding reciprocal-lattice point.

Let us now consider a given reciprocal-lattice point hkl at a distance $\sigma < 2$ from the origin O. The locus of this point, as the crystal is made to execute any arbitrary rotation, lies on a sphere of radius σ centered at O. The point P for the hkl reflection may therefore be chosen anywhere on the circle in which this sphere intersects the sphere of reflection, both the crystal and counter orientations depending on this choice. Furthermore, even with P fixed, the crystal orientation is not yet uniquely specified since the lattice is still free to rotate about the line OP without violating the conditions for reflection. The choice of the crystal setting for a given reflection is thus subject to a double indeterminateness, which arises from the fact that the crystal possesses three rotational degrees of freedom while the Bragg relation imposes only a single restraint upon its orientation. If we consider, moreover, that we are free to choose, in an almost unlimited number of ways, the sequence in which the reflections are to be recorded, it is evident that the crystal and counter motions may vary widely in different possible spectrometer designs. Our problem, then, is to find a particular combination of crystal and counter motions that satisfies the basic requirements in the simplest and most convenient manner.

GENERAL SCANNING PROCEDURE

A useful way to approach the solution of this problem is to imagine the crystal rotating about a fixed axis, which for simplicity we shall take parallel to one of the axes of the crystal lattice, say the b axis. By thus restricting its motion to a simple rotation, we allow the crystal only one degree of freedom and the indeterminateness accordingly disappears. Let us first confine our attention to the zero layer, consisting of all the $h0l$ reflections, for which it is convenient, as with photographic recording, to set the b axis, the rotation axis, perpendicular to the incident beam. As the crystal rotates, all the zero-layer reciprocal-lattice points cut the sphere of reflection on its equator, and thus the corresponding reflections all lie in the equatorial plane perpendicular to the rotation axis. However, these reflections occur in a thoroughly irrational sequence; that is, the time order in which the reciprocal-lattice points cut the sphere of reflection is not related in any simple manner to their crystallographic indices, h and l, or to the Bragg angle ϑ, or to any other readily-determined parameter that may be assigned to them. If we, then, let the crystal rotate and attempt to record all the zero-layer reflections as they come up, we shall be faced with the awkward task of determining the instant at which each reciprocal-lattice point cuts the sphere of reflection and of setting the counter tube in the proper place at the proper time for measuring each reflection. This is an entirely possible procedure, but it seriously violates condition 2 above.

To overcome this objection we shall divide the zero-layer reflections into groups such that the reflections in each group occur systematically as the crystal rotates about its b axis. Consider, for example, a set of reciprocal-lattice points lying on a straight line in the zero-layer plane. Each point is characterized by the coordinate giving its position on the line, and both the crystal and counter orientations necessary for recording the corresponding reflection may be expressed as functions of this coordinate and of the parameters specifying the position of the line itself. For each line a mechanically feasible combination of crystal and counter rotations is possible if we take the successive points in the order of their positions along the line. The simplification thus attained depends, of course, on the manner in which these lines in reciprocal space are chosen. The most suitable choice is the obvious one of taking the lines parallel to one of the reciprocal axes. Its principal advantages are that the sequence of reflections is rational in terms of the crystallographic indices, the spacing of the reciprocal-lattice points constant for all lines, and the number of lines to be scanned relatively small. An alternative procedure would be to take the reciprocal-lattice points in radial lines through the origin, each such line representing successive orders of reflection from a basal set of crystal planes. This method has the advantage that it permits the counter and crystal to rotate at a fixed two-to-one ratio. We nevertheless reject it because of the variation, from line to line, in the spacing of the reciprocal-lattice points and, especially, because of the large number of separate lines to be scanned. In any case, the advantage of the two-to-one rotation ratio is not restricted to this particular procedure; it has, in fact, been retained in one of the methods described below for scanning the reciprocal lattice in parallel lines.

While only the zero layer has been discussed, the conclusions we have reached may be readily generalized to include upper-layer reflections as well. The normal-beam method is not, however, satis-

factory for the upper layers since it does not fulfill condition 1. Thus the b axis cannot, in general, remain normal to the incident beam, nor will the same rotation axis necessarily be chosen for all reflections. But the argument for scanning the reciprocal lattice in a series of straight lines parallel to one of the reciprocal axes remains valid in the three-dimensional case, where the objections to the choice of radial lines are even stronger than in the zero-layer problem.

Accordingly we shall now direct our attention to possible methods of scanning a set of parallel straight lines in reciprocal space, these lines being taken, for the purpose of the following discussion, parallel to the reciprocal c^* axis. The several methods to be discussed will differ from one another primarily in the position, relative to the sphere of reflection, in which each of these lines is scanned.

EQUATORIAL METHOD

One possibility is to adapt the basic procedure outlined above for the zero layer, so that it can be applied, with slight modifications, to the entire reciprocal lattice. Thus we retain the advantage of the one-circle counter motion so that the counter tube can, for example, be made to run on a horizontal circular track around the crystal. This arrangement is especially advantageous if a pre-amplifier and a heavy cable must travel along with the counter tube, or if the Geiger counter is to be replaced by the heavier and bulkier scintillation counter. Also it may obviate the necessity of constructing an entirely new instrument by permitting the use of a standard powder spectrometer with relatively minor alterations.

The method involves, for each reciprocal-lattice line (hk-), two operations, which may be designated [A] and [B]. In [A] the line (hk-) is brought into a suitable position in the horizontal equatorial plane of the sphere of reflection, the plane that originally was occupied by the zero layer. In [B] the successive reciprocal-lattice points on (hk-) are brought in turn onto the sphere of reflection and the reflected intensities measured.

Let the crystal be mounted with the c^* axis horizontal and initially perpendicular to the incident beam, also horizontal. In order to define its initial orientation more completely, we may consider the b axis of the crystal to be vertical with its positive direction pointing upwards (Figure 1). For each line (hk-), step [A] consists of a rotation of the crystal about the horizontal c^* axis through an angle φ, which is the angle at which the normal to (hk-) from the reciprocal-lattice origin is inclined to the horizontal. As will be clear from the figure, this step is superfluous when $k = 0$; lines ($h0$-) in the zero layer are already in correct scanning position. Thus each line, whether in the zero layer or any upper

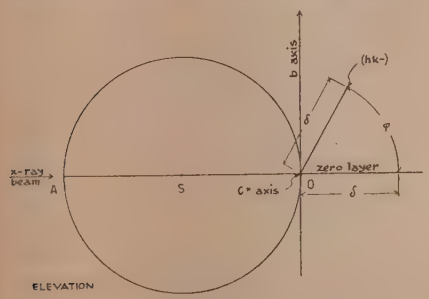


Figure 1
Bringing line (hk-) into position for scanning by equatorial method.

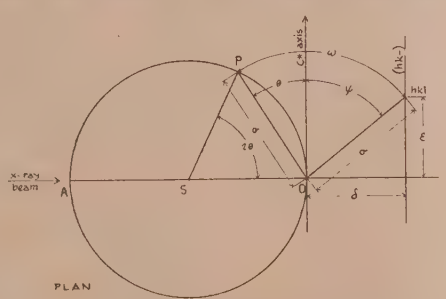


Figure 2
Measurement of hkl reflection by equatorial method.

layer of the reciprocal lattice, lies, after step [A], in the equatorial plane of the sphere of reflection and perpendicular to the incident beam. From this position it is scanned, in step [B], by means of a horizontal rotation of the crystal, which brings each reciprocal-lattice point on the line, in turn, onto the equator of the sphere of reflection. Thus to bring a given point hkl, at a distance σ from the origin (Figure 2), onto the sphere of reflection, the crystal must be rotated through an angle $\omega = \psi + \vartheta$, where ψ is the angle between the radius vector to hkl and the c^* axis, and ϑ the Bragg angle defined by the equation: $2 \sin \vartheta = \sigma$.

The axis of the counter cylinder must be rotated meanwhile into a position parallel to SP at an angle 2ϑ to the direct beam. In this manner the reflections represented by the line (hk-) are measured con-

secutively, the process being repeated for successive lines until all available Bragg reflections have been recorded.

The scanning of the entire reciprocal lattice, line by line, thus requires the evaluation of three parameters, φ, ψ, and ϑ, of which the first, needed for step [A] only, must be determined once for each upper-level line, while the other two are different for each reflection. For these two, at least, analytical computation and individual hand setting would be extremely laborious, and it is therefore desirable to incorporate into the instrument either a suitably-calibrated cam-and-follower device, by which the required motions would be coordinated mechanically, or else a linkage mechanism, which would allow the operator to set the appropriate angles automatically by working directly from a plot of the reciprocal lattice. In terms of the cylindrical coordinates, δ and ε, respectively perpendicular and parallel to the c^* axis, the required angles are defined by the equations:

$$tan\ \psi = \delta/\varepsilon\,;\ 2\ \sin\ \vartheta = (\delta^2 + \varepsilon^2)^{1/2}.$$

These cylindrical coordinates are selected as most convenient for describing the position of each reciprocal-lattice point, since δ is constant for each line (hk-) and ε varies by equal increments in passing from point to point along any line. For a monoclinic crystal, they are given by the equations:

$$\delta = [(kb^*)^2 + (ha^* \sin\beta^*)^2]^{1/2};$$

$$\varepsilon = lc^* + ha^* \cos\beta^*, \tag{1}$$

while φ, which is the third cylindrical coordinate, may be found from the equation:

$$\sin\ \varphi = kb^*/\delta. \tag{2}$$

EQUI-INCLINATION METHOD

A somewhat different procedure, using an equi-inclination crystal rotation, involves only a one-circle crystal motion for each entire reciprocal-lattice level, but requires the counter tube to travel in cones, different for each level. In this method, the crystal is initially mounted, as in the equatorial method described above, with its b axis vertical and the reciprocal c^* axis horizontal and normal to the incident beam, also assumed to be horizontal.

The zero level is scanned in precisely the same manner as in the equatorial method, with the crystal and counter tube rotating about the vertical b axis. For upper levels too, in this method, the crystal and counter rotate about the b axis, which, however, is inclined at a different angle for each level. In practice, the basic settings of the crystal and counter are adjusted once for an entire reciprocal-lattice level in a preliminary operation, which we may call [A'], after which the scanning of each line in that level requires only a one-step procedure. Thus in step [A'], the crystal is rotated about the horizontal c^* axis through an angle ν (Figure 3) such that $2\ \sin\ \nu = \zeta$, where $\zeta = k\lambda/b$ is the perpendicular height of the kth level above the reciprocal-lattice origin. As a result of this vertical rotation, the kth level, now inclined at an angle ν to the horizontal, intersects the sphere of reflection in a circle of radius $r = \cos\ \nu$, which is the reflecting circle for this level (Figure 4). The intersection of the b axis with the kth-level plane, which in crystals of monoclinic or higher symmetry is the reciprocal-lattice point $0k0$, lies on the reflecting circle at the point O', in the vertical plane through SO, such that the radius SO' makes an angle of 2ν with SO. Also in step [A'], the counter axis is inclined out of the horizontal plane so as to lie initially parallel to SO'. The kth level is now in position for the successive scanning of its various lines (hk-). This is, for each line, step [B], in which the crystal and counter must both be free to rotate about the inclined b axis, and the procedure closely resembles that followed for the zero layer. A given recipro-

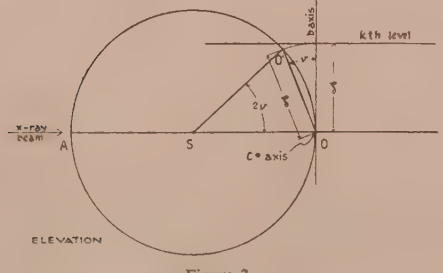


Figure 3.
Bringing kth level into position for scanning by equi-inclination method.

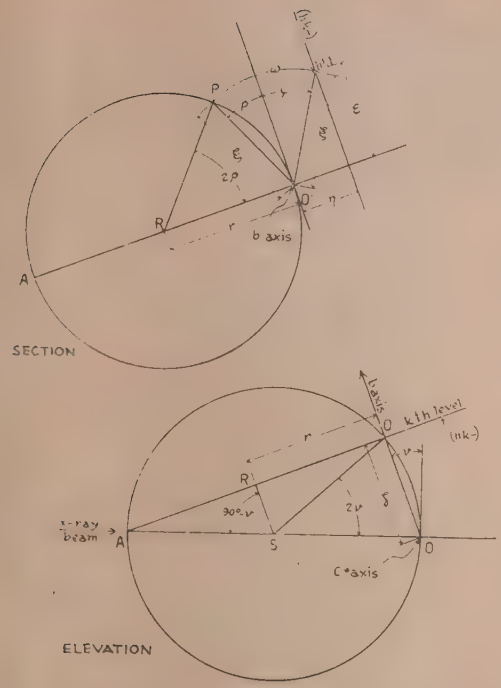


Figure 4
Measurement of *hkl* reflection by equi-inclination method.

cal-lattice point *hkl*, at a distance ξ from O', requires a crystal rotation of $\omega = \psi + \varrho$ and a counter rotation of 2ϱ, where ψ is the angle between the vector from O' to *hkl* and the tangent to the reflecting circle at O', and ϱ is defined by the equation: $2r \sin \varrho = \xi$. The axis of the counter cylinder, making a fixed angle 90°—ν with the *b* axis, itself inclined at an angle ν to the vertical, generates a tilted circular cone of apex angle 180° — 2ν, tangent to the path of the incident beam.

In this, as in the equatorial method, the rotation angles of the crystal and counter vary from point to point throughout the reciprocal lattice and therefore require some automatic mechanism for their evaluation if tedious computations are to be avoided. A somewhat more elaborate device is needed here, because the radius of the reflecting circle is different for each level. The equations defining the necessary angles are: $\tan \psi = \eta/\varepsilon$; $2r \sin \varrho = (\eta^2 + \varepsilon^2)^{1/2}$, where η and ε are the orthogonal coordinates of the reciprocal-lattice point in the plane of the *k*th level and may be readily determined from a plot of the a^*-c^* reciprocal net. An expression for ε, valid for a monoclinic crystal, has been given above in (1); the corresponding expression for η is: $\eta = ha^* \sin\beta^*$.

The major advantage of the equi-inclination method is the fact that the angle ν is fixed for each reciprocal-lattice level, unlike the angle φ in the equatorial method, which must be reset for each line except in the zero level. Consequently the motions involved in the scanning of each level are simpler in the equi-inclination method. A further consequence becomes apparent when absorption corrections are to be made. For, if the crystal may be regarded as approximately cylindrical, it should be possible to derive a satisfactory correction factor that will depend only on the relative orientations of the incident and reflected beams and of the cylinder axis. By taking the cylinder axis as the *b* axis of the foregoing discussion, one can arrange to keep its inclination to the primary beam constant for each level, in which, therefore, the required correction will be a function of ϑ only.

TANGENT METHOD

The last method to be considered ignores the division of the reciprocal lattice into zero and upper levels and requires, again, a two-step procedure for each line. The second step, this time, is a simple two-to-one

rotation of the counter and crystal, which we make possible by having the line that is to be scanned intersect the rotation axis on the sphere of reflection.

The similarity of this method to the others is most apparent if we again consider the c^* axis to be set initially horizontal and normal to the incident beam. The reciprocal lattice is scanned, as before, in lines (hk-) parallel to the c^* axis. This time, however, a different reflecting circle on the sphere of reflection is used for each line. To bring a given line (hk-) into scanning position, the crystal is rotated, in step [A], about the horizontal c^* axis through an angle τ (Figure 5) such that (hk-) becomes tangent to the sphere of reflection.

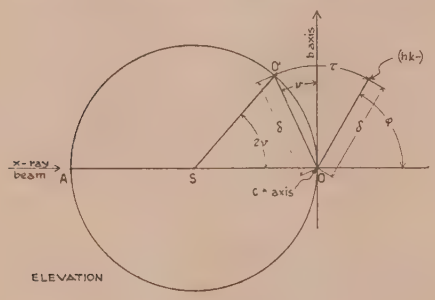
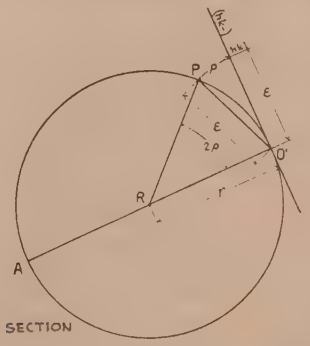


Figure 5 — Bringing line (hk-) into position for scanning by tangent method.

The point of tangency O' lies in the vertical plane through SO, and the radius SO' makes an angle 2ν with SO, where ν is defined by the equation:

$$2 \sin \nu = \delta, \qquad (3)$$

δ being the perpendicular distance from the origin to the line (hk-). For this line, the reflecting circle lies in the plane perpendicular to OO' at O' and has a radius $r = \cos \nu$ (Figure 6). The counter axis, meanwhile, is inclined at an angle 2ν to the horizontal so that it lies initially parallel to SO'. In step [B] both the crystal and the counter are rotated about an axis parallel to OO', which makes an angle ν with the vertical. To bring the point hkl, at a distance ε from O', onto the reflecting circle, the crystal must rotate through an angle ϱ such that $2r \sin \varrho = \varepsilon$. The axis of the counter, in order to reach a position parallel to SP, must rotate through an angle 2ϱ. Thus it is possible to gear together the crystal and counter motions about the common rotation axis in such a way that the counter always rotates at twice the angular rate of the crystal. Then as each reciprocal-lattice point is brought onto the reflecting circle, the counter axis will automatically be brought into position to intercept the reflected beam. It is this permanent two-to-one ratio of the counter and crystal rotations that constitutes the peculiar advantage of the tangent method. As in the equi-inclination method, the axis of the rotating counter generates a circular cone of apex angle $180° - 2\nu$.



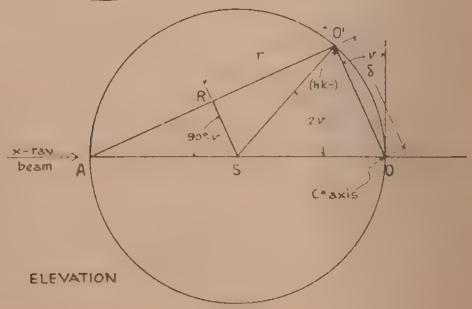


Figure 6
Measurement of hkl reflection by tangent method.

We may notice, incidentally, that for other than triclinic crystals, the $0kl$ reflections are measured similarly in the equi-inclination and tangent methods.

In the tangent method, the scanning operation depends upon the determination of the three parameters τ, ν, and ϱ, of which the first two are required only for step [A] and need therefore be determined only once for each line. The third parameter, ϱ, varies from point to point throughout the reciprocal lattice; we envisage a linkage mechanism that will automatically compute this angle from the cylindrical coordinates, δ and ε, of each reciprocal-lattice point. Both τ and ν may, without too great an effort, be either analytically or graphically evaluated and hand set if one wishes to avoid the use of two separate linkage devices. The angle ν is given by equation (3): τ may be derived as $90^\circ - \eta' + \nu$, where η' is defined by equation (2).

It is readily seen that none of the three methods described imposes any restrictions on the range of reflections that can be measured, beyond those that inevitably arise from the physical impossibility of recording the very-high-angle back reflections.

The principal features of the three methods described are summarized in Table I.

TABLE I

Comparison of the three scanning methods

Method		Setting Parameters	Major Advantage
Equatorial	Step [A]:	$\varphi = \sin^{-1}(\zeta/\delta)$	One-circle counter travel
	Step [B]:	$\psi = \tan^{-1}(\delta/\varepsilon)$	
		$\vartheta = \sin^{-1}(\sigma/2)$	
Equi-inclination	Step [A']:	$\nu = \sin^{-1}(\zeta/2)$	One-step procedure for lines of each
	Step [B]:	$\psi = \tan^{-1}(\eta/\varepsilon)$	reciprocal-lattice level
		$\varrho = \sin^{-1}(\xi/2 \cos \nu)$	
Tangent	Step [A]:	$\nu = \sin^{-1}(\delta/2)$	Two-to-one rotation of counter and
		$\tau = \sin^{-1}(\delta/2) + \cos^{-1}(\zeta/\delta)$	crystal
	Step [B]:	$\varrho = \sin^{-1}(\varepsilon/2 \cos \nu)$	

ζ, ε, and η are the orthogonal coordinates of the reciprocal-lattice point hkl. ζ is measured parallel to the b axis; ε, parallel to the c^* axis; and η, perpendicular to both. The other coordinates used are: $\delta = (\zeta^2 + \eta^2)^{1/2}$; $\xi = (\varepsilon^2 + \eta^2)^{1/2}$; $\sigma = (\zeta^2 + \varepsilon^2 + \eta^2)^{1/2}$.

INTEGRATED INTENSITIES

Although the Geiger counter can measure only one reflection at a time, it is nevertheless possible in principle, and in some respects desirable, to scan each line (hk-) with a continuous motion of both the crystal and the counter tube, by any of the methods described, so as to carry the reciprocal-lattice points successively through the sphere of reflection and thus automatically integrate the corresponding reflections. The integrated intensities could be measured either with a continuously-recording counting-rate meter or with a scaler that could be read and reset after each count. Such a procedure, however, would be extremely slow since only a small fraction of the total scanning time for each line would be used for the actual intensity measurements, the remainder being consumed in the slow rotation of the crystal and counter tube between successive reflecting positions. For most purpose this is a very unsatisfactory arrangement. It is usually preferable to bring each reciprocal-lattice point rapidly onto the sphere of reflection and then to hold it there during the time needed for the measurement of the reflected intensity. But this procedure does not solve the problem of measuring integrated, rather than peak, intensities. An obvious expedient is to rotate or oscillate the crystal slowly through a small range about the Bragg angle, somewhat in the manner of Wooster and Martin's ionization spectrometer[3]. However, it appears simpler to keep the crystal stationary and to use a plane-convergent x-ray beam to produce essentially the same result. This device of, in effect, oscillating the incident

beam rather than the crystal was used by Kratky[4] for the photographic determination of the lattice constants of small crystals and has recently been suggested by Cochran[5] for intensity measurements with a Geiger counter. It requires an extended x-ray target whose length subtends at the crystal an angle somewhat larger than the mosaic spread of the crystal. Besides its simplicity, it has the further advantage that it yields a constant counting rate for each reflection (apart from the effect of the pulsating output from the x-ray tube, which can be measured and allowed for), so that the correction for resolving-time losses in the counter may be more easily determined than in the rotating-crystal methods.

Because the integrated intensities measured in this way are equivalent to those produced by a rotating crystal, they must be corrected by the usual Lorentz factor, computed for the case of a rotation axis perpendicular to the plane of x-ray convergence. If the plane of convergence is horizontal, the corresponding rotating-crystal method is one in which the rotation axis is vertical. Thus for the equatorial method described above, in which every point of the reciprocal lattice is recorded on the horizontal equator of the sphere of reflection, the required correction, with a horizontally-convergent x-ray beam, has everywhere the same form as for the zero-layer reflections in a normal-beam rotation photograph; the measured intensities must each be multiplied by $\sin 2\vartheta$. In the equi-inclination and tangent methods, however, the reflections are not restricted to the equatorial plane, and thus the intensities must be further multiplied by the level factor, $[1-(\sin \varkappa/\sin 2\vartheta)^2]^{1/2}$, in which $\varkappa$ is the angle between the reflected beam and the plane of convergence of the incident beam. This expression for the level factor was first given by Ott[6] and is more appropriate for our purpose than the more familiar form in which it was later derived by Cox and Shaw[7]. The complete Lorentz correction, then, is

$$1/L = \sin 2\vartheta[1-(\sin \varkappa/\sin 2\vartheta)^2]^{1/2} = (\sin^2 2\vartheta - \sin^2 x)^{1/2}. \tag{4}$$

If the plane of convergence is horizontal, it can readily be shown that $\sin \varkappa = \sin 2\nu \cos^2 \varrho$, and we may substitute this expression in equation (4) so as to obtain

$$1/L = (\sin^2 2\vartheta - \sin^2 2\nu \cos^4 \varrho)^{1/2}.$$

But since

$$\cos \vartheta = \cos \nu \cos \varrho, \tag{5}$$

as may be seen from the equations defining these angles, we may eliminate either ϱ or ϑ to derive the alternative expressions:

$$\begin{aligned} 1/L &= 2 \cos \vartheta (\tan^2 \vartheta - \tan^2 \nu)^{1/2} \\ &= \cos \nu \sin 2\varrho. \end{aligned}$$

From the latter form it is immediately evident that the method will fail whenever $\varrho = 0$, for the factor $1/L$ then vanishes. In the equi-inclination method, $\varrho = 0$ for all the $0k0$ reflections with other than triclinic crystals, while in the tangent method this occurs for the entire $hk0$ zone. Consequently, either these reflections will have to be measured in some other way or a more exact formula for the Lorentz correction, such as that of Heide[8], will have to be applied.

If a vertically-convergent beam is used, $\sin \varkappa = \cos \nu \sin 2\varrho$, and on substituting this expression in equation (4), we obtain $1/L = (\sin^2 2\vartheta - \cos^2 \nu \sin^2 2\varrho)^{1/2}$.

Again we may make use of (5) and so derive the alternative forms:

$$\begin{aligned} 1/L &= 2 \cos^2 \vartheta \tan \nu \\ &= \sin 2\nu \cos^2 \varrho. \end{aligned}$$

In this case $1/L$ vanishes when $\nu = 0$, as it does for all reflections in the equatorial method and for the zero layer in the equi-inclination method. In the tangent method, only the $00l$ reflections are affected and thus require separate treatment.

We may conclude that the equatorial and equi-inclination methods require a horizontally-convergent x-ray beam, but that a vertical plane of convergence is preferable for the tangent method. The distinc-

tion between horizontal and vertical must, of course, be understood relative to the descriptions of the various methods given above. If, for example, it is desired to use the tangent method with an x-ray tube that provides a horizontally-convergent beam, it is necessary merely to rotate the entire spectrometer through 90° so that all the reflecting circles are vertical; the result will then be equivalent to the use of a horizontal plane of convergence with the tangent method as described above.

REFERENCES

1. Cochran, W., 1951, *Acta Cryst.*, **4**, 81.
2. Buerger, M. J., 1942, *X-Ray Crystallography*, John Wiley and Sons, New York.
3. Wooster, W. A., and Martin, A. J. P., 1936, *Proc. Roy. Soc.*, **A155**, 150.
4. Kratky, O., 1930, *Zeits. f. Krist.*, **A73**, 567 and subsequent papers.
5. Cochran, W., 1950, *Acta Cryst.*, **3**, 268.
6. Ott, H., 1924, *Zeits. f. Physik*, **22**, 201.
7. Cox, E. G. and Shaw, W. F. B., 1930, *Proc. Roy. Soc.*, **A127**, 71.
8. Heide, H. G., 1951, *Acta Cryst.*, **4**, 29.

CATALYSED SOLID-SOLID OXIDATION REACTIONS

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INTRODUCTION

While the reaction of various forms of carbon with gaseous oxidants is one of the most thoroughly investigated phenomena in chemistry, only a very little is known about the reaction of carbon with solid oxidants[1-7], and even less about the influence of catalysts on this reaction[2].

Undoubtedly this reaction is composed of a number of steps, one of the most important of them being the solid-solid pre-ignition reaction, from which the oxidation proper develops layer by layer. The present study is devoted to the influence of various chemical and physical factors on this solid-solid reaction, and in particular to the catalysed oxidation of carbon black, nuchar and graphite as well as of a number of polymers by solid potassium perchlorate.

EXPERIMENTAL

Apparatus

Two different forms of apparatus, both described in earlier papers[6,8] were used for the measurement of the evolution of carbon dioxide.

Materials used

Potassium perchlorate and all the catalysts (with the exception of lithium bromide) were commercial products of analytical grade. The carbon black (average diameter of particles: 0.005 mm) contained 0.5% volatile matter at 300°C, in vacuo, and 1.5% ash, consisting mainly of alkali sulphates and traces of iron oxide. The nuchar (Eastman Kodak Co., average diameter of particles: 0.01 mm) contained 3.5% ash, of which 0.45% was iron oxide, 0.56% silicon dioxide and 2.5% calcium sulphate. The graphite (av. particle diameter: 0.05 mm) contained 3.4% ash, of which 2% was iron oxide and the balance silicates.

The following polymers were used:

Polystyrene was prepared from redistilled commercial styrene with the addition of 0.25% of dibenzoyl peroxide, styrene copolymers with 10% of *p*-divinyl-benzene or 10% of 4,4′-diisopropenylbiphenyl[9]. Bakelite and Novolac were prepared according to known procedures[11,10].

Preparation of samples

Potassium perchlorate and the catalysts were ground to pass a 200 mesh sieve, the polymers as far as possible, to pass a 130 mesh sieve. Otherwise fine shavings were made on a lathe and these shavings cut by razor blades until they passed a 30 mesh sieve. The potassium perchlorate was mixed with the polymer or carbon in stoichiometric ratios, calculated on the basis of carbon dioxide and water (with polymers) or carbon dioxide alone (with carbon) being the products of the reaction. For each mole of carbon, 0.05 equivalents of the different catalysts were used (*e.g.* 0.05 moles of potassium chloride, 0.025 moles of barium chloride etc.). One gram portions of the thoroughly mixed reaction mixtures were pressed into tablets of 20 mm diameter, under a pressure of 2250 atmospheres.

The *experimental procedure* has been described previously[6,8]. The weight of the samples was chosen so as to contain 12 mg of carbon (about 82-84 mg). The weight loss of the samples corresponded to that calculated on the basis of carbon dioxide being the only gaseous product of the reaction; indeed, in all cases in which the amount of gas sufficed for analysis, it was found to consist of carbon dioxide only, and was quantitatively equivalent to the amount of potassium chloride found in the residue.

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Experiments with polymers

Polystyrene. No reaction took place between polystyrene and potassium perchlorate, as the polymer depolymerised and distilled out from the reaction chamber. In the interval of 300-550°, the styrene vapour did not react with potassium perchlorate.

Styrene copolymers reacted very slowly with potassium perchlorate in the temperature range of 360-400°C, and partial depolymerization took place at the same time. The addition of potassium carbonate had no effect on the reaction; lithium chloride accelerated it. In the case of styrene-diisopropenylbiphenyl, in the presence of lithium chloride the pressure in the apparatus at 390° corresponded after five hours to about 40% reaction. The reproducibility of the experiments was unsatisfactory.

Bakelite and Novolac. Bakelite reacted at 367° with potassium perchlorate to the extent of about 15% in the course of five hours. Potassium carbonate inhibited this reaction. In the presence of lithium chloride, the reaction mixture ignited after 2-3 minutes, the pressure developed corresponding to about 50% reaction. At 343°, about 40% reacted in five hours, and about 70% in twenty-five hours.

Novolac reacted with potassium perchlorate at 367° to the extent of about 30% in the course of five hours. In the presence of lithium chloride the mixture ignited at 355°C. At 343°, the reaction was similar to that of bakelite. In contrast to the results with bakelite, potassium carbonate acted as a catalyst, giving very similar reaction rates to lithium chloride, even causing ignition at 367°.

Experiments with carbon black

The rate of the reaction between carbon black and potassium perchlorate was measured, at 343°, without catalyst and in the presence of lithium, barium, potassium and sodium chloride, potassium iodide and lithium carbonate (Figure 1). In the presence of lithium bromide the sample ignited. Analogous experiments, (not shown in Figure 1), were made with potassium bromide, which had the same effect as sodium chloride; potassium sulphate, aluminium oxide, lithium sulphate and talcum gave about the same curves as the experiment without catalyst; magnesium chloride and potassium carbonate caused a very slight, and both potassium orthophosphate and metaphosphate a strong inhibition effect, about equal to that produced by lithium carbonate. In the experiment with potassium iodide, iodine vapour condensed in the cold part of the apparatus: the sigmoid reaction curve obtained may therefore be due to the decomposition of potassium iodide, which seems to inhibit the reaction strongly before its decomposition, and almost not at all after it. The reproducibility of the experiments was fairly satisfactory (about 1-2%).

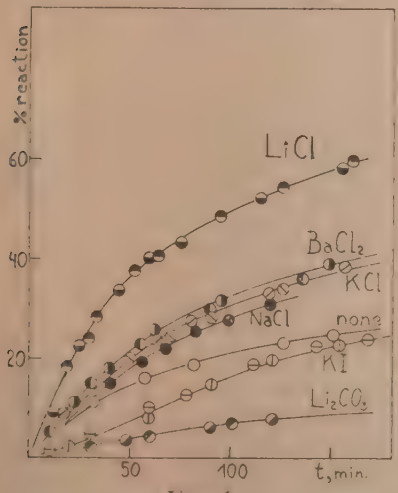

Figure 1

Reaction rates of one mole of carbon black with 0.5 *mole of potassium perchlorate* (80 *mg samples*) *at* 343° *in the presence of various salts. Different signs near each curve represent duplicate experiments.*

The reaction velocity at temperatures very near to the ignition point of the mixtures was strongly dependent on the size of the sample. With lithium bromide as the catalyst, standard size samples ignited in every case at 343°, and gave about the same curves as the samples with lithium chloride at 343°, while samples half the standard amount (about 49 mg) gave about the same curves at 343° as standard samples with barium chloride at the same temperature.

Experiments with nuchar

The rates of the reaction of nuchar with potassium perchlorate were measured at 320° without catalyst and in the presence of lithium bromide, potassium bromide and potassium orthophosphate (Figure 2). Potassium carbonate had practically no effect, potassium chloride and iodide inhibited the reaction to the same extent as the bromide. In the presence of lithium chloride, the mixture ignited at 320°, at 317° it gave about the same curve as lithium bromide at 320°. The reproducibility of the experiments varied from 1% (without catalyst) to 3% (with potassium iodide).

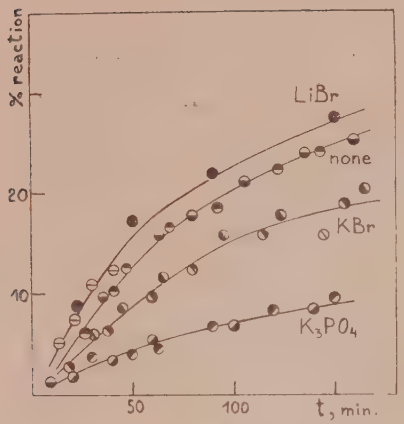

Figure 2

Reaction rates of one mole of nuchar with 0.5 mole of potassium perchlorate (80 mg samples), at 320° in the presence of various salts.

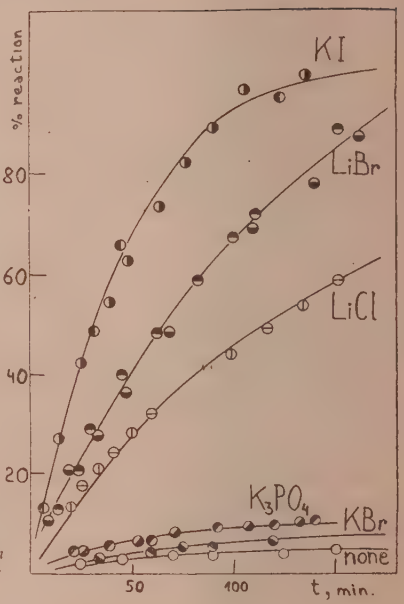

Figure 3

Reaction rate of one mole of graphite with 0.5 mole of potassium perchlorate (80 mg samples), at 450° in the presence of various salts.

Experiments with graphite

The reaction rates of potassium perchlorate with graphite were measured at 450° without catalyst and in the presence of potassium iodide, bromide and orthophosphate, and of lithium bromide and chloride. Potassium metaphosphate and carbonate gave about the same reaction rates as the bromide, while potassium chloride had no effect. The reproducibility of the experiments was about 2%, except in the case of lithium chloride, in which variations of as much as 20% were observed. (The curve for lithium chloride in Figure 3 was chosen so as to represent an approximate average of six experiments).

None of the substances studied was found to inhibit the reaction with graphite. As in the case of carbon black, potassium iodide decomposed during the reaction and iodine vapour condensed on the cold parts of the apparatus.

DISCUSSION

Kinetics of the reaction

The experiments with the different polymers were not sufficiently reproducible to allow a quantitative interpretation of the data. In the following discussion, only the experiments made with the three different forms of carbon have been considered.

In view of the relatively low temperatures of the experiments, which even in the case of graphite lie well below the temperature of decomposition of potassium perchlorate (510°C)[12], there can be no doubt that the reactions described are genuine solid-solid ones. In a previous communication[6] the curves of the oxidation of carbon black by potassium perchlorate have been shown to conform to two kinetic equations,

$$dx/dt = k(a-x)(b-x) \qquad (1)$$

at the beginning, and

$$dx/dt = k(a-x)(b-x)/0.5x \qquad (2)$$

in the second part. The factor $1/0.5x$ is appearing as due to the inhibiting influence of the potassium chloride formed in the course of the reaction. It has been found that it is possible to apply to the results the equation of Jander[13]

$$dy/dt = k/y \qquad (3)$$

(y is the thickness of the product layer between the two reactants) and its integrated form,

$$y^2 = 2kt \tag{3a}$$

or

$$kt = \left[1 - \sqrt[3]{(100 - x)/100}\right]^2 \tag{3b}$$

in which the thickness of the product layer is expressed by means of the amount of the reaction product x and the initial radius of the grains of the reactants r is incorporated into the rate-constant k. According to Jander, (3b) can be used when one of the reactants is in a great excess and x is taken as the percentage of the minor constituent which has reacted at time t. In the present case the two reactants were taken in equivalent stoichiometric amounts, as however the surface area of the carbon is much larger than that of the perchlorate, the same equation should be applicable at least for the beginning and probably also for the bulk of the reaction.

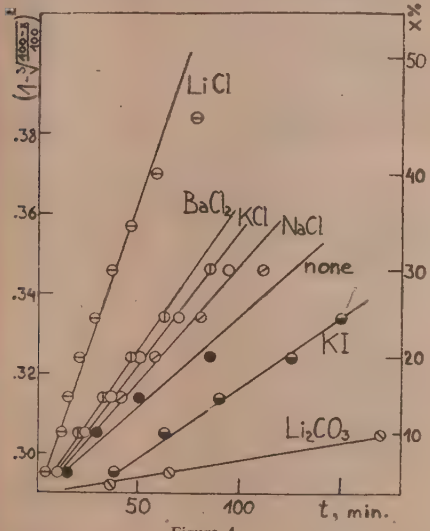

Figure 4
Values of kt *against time, calculated from* (3b), *for mixtures with carbon black at* 343°

In Figures 4—6, the values of $\left[1 - \sqrt[3]{(100 - x)/100}\right]^2$ are plotted against the corresponding values of t for various mixtures with carbon black, nuchar and graphite, respectively. In all cases the experimental points lie on a straight line in the first part of each reaction, and the deviation becomes marked only as the reaction velocity has fallen to about one third of the initial value. Even so the relationship holds well for carbon black (Figure 4) in the presence of lithium chloride up to 40% and in the presence of most other catalysts up to 20—25% reaction. With nuchar, the rates were generally slow and deviation from the straight lines appears already after 15-20% reaction. With graphite, in the presence of the three most effective catalysts (potassium iodide, lithium bromide and chloride) the equation holds well up to 65—70% and is again less satisfactory for the less effective catalysts.

The relative values of the rate constants, as calculated from Figures 4—6, are given in Tables I—III, in which the rate of the corresponding uncatalysed reaction is arbitrarily taken as unity.

In a genuine solid-solid reaction between two plane reactant surfaces pressed together, the main rate-determining factor is the transport of material by diffusion through the product layer. When the reactants are initially in the form of powders pressed together, the reaction is probably also propagated by migration of molecules from points on the surface of one reactant, but not in contact with the other, to the points of contact, as well as by self diffusion of the molecules from the interior of the reactants to the surface. The temperature, where self diffusion in a salt is beginning to be effective, according to Tamman[14], is about 0.5 T_m (T_m = melting point of the salt in ° K); in all our experiments the reaction temperature was well above Tamman's value.

Now whatever the mechanism of the reaction may be, and whatever modes of material transport have to be taken in account, any catalyst enhancing the velocity of a solid-solid reaction must necessarily act at the same time also as a physical barrier between the reactants, inhibiting the reaction to a certain extent*.

If, however, the mechanically inhibiting influence of the catalyst can be taken as constant throughout the reaction, or at least in its first part, this will influence only the absolute value of the rate constant, and the mathematical form of (3b) will not change. Possibly, therefore, the deviation of the experimental values from the theoretical equation at the later stages of the reaction is due to the relatively increasing inhibition by the catalyst.

* This must be true for all cases, unless the catalyst is in a molecularly divided state in one of the reactants (e.g. in a solid solution), which certainly does not apply to our experiments.

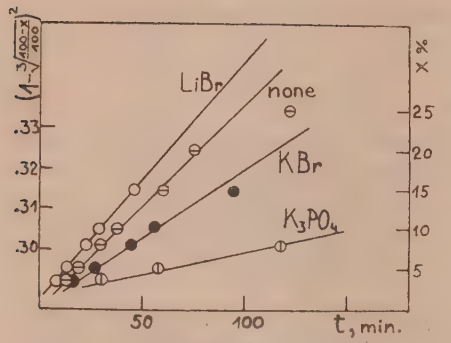

Figure 5

Values of kt *against time, calculated from* (3b), *for different mixtures with nuchar, at* 320°

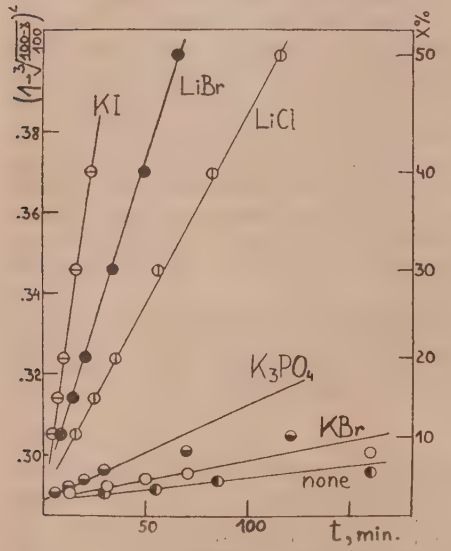

Figure 6

Values of kt *against time, calculated from* (3b), *for different mixtures with graphite, at* 450°

TABLE I

Relative reaction rates for the oxidation of carbon black by potassium perchlorate in the presence of various salts at 343°

Substance added	*Rate*
Lithium bromide	∞ (ignition)
Lithium chloride	3.27
Barium chloride	1.65
Potassium chloride	1.53
Sodium chloride Potassium bromide	1.29
None	1.00
Potassium sulphate Lithium sulphate Aluminium oxide Talcum	1.0
Potassium carbonate Potassium iodide Magnesium chloride	0.9
Lithium carbonate Potassium orthophosphate Potassium metaphosphate	0.2

TABLE II

Relative reaction rates for the oxidation of nuchar by potassium perchlorate in the presence of various salts at 320°

Substance added	*Rate*
Lithium chloride	∞ (ignition)
Lithium bromide	1.16
None	1.00
Potassium carbonate	1.0
Potassium chloride Potassium bromide Potassium iodide	0.7
Potassium orthophosphate	0.25

TABLE III

Relative reaction rates for the oxidation of graphite by potassium perchlorate in the presence of various salts at 450°

Substance added	*Rate*
Potassium iodide	57.0
Lithium bromide	24.6
Lithium chloride	14.8*
Potassium orthophosphate	3.55
Potassium metaphosphate Potassium bromide	1.38
Potassium carbonate	1.23
None	1.00
Potassium chloride	1.0

* Average value of six experiments.

The mode of action of the catalysts

In a reaction between two solid substances, a catalyst could conceivably exert its influence in the following ways:

a) The catalyst may lower the melting point of either of the reacting substances sufficiently to effect an at least local sintering of the solid surface, and, by doing so, enlarge the contact area between the two substances. In this case the reaction will be of the solid-liquid and not genuinely of the solid-solid type[13].

b) The catalyst may, with partial migration into either of the reacting substances, deform their crystalline structure and cause an increase in the number of active patches[15] on the surface and weaken the valence bonds of the reacting atoms. In this case, the effect of a catalyst on solid-solid reactions would parallel that of catalysts of the thermal decomposition of solids[16-21].

c) The catalyst may participate in the transition complex of the two reactants, and thus lower the energy of activation needed for the formation of this complex, or it may participate in the reaction in the form of an unstable oxygenated intermediate, thus serving as an oxygen carrier[22-23].

As already pointed out, case a) can be eliminated, as it was shown in a previous paper[6] that the temperature of the sample does not rise appreciably above the measured temperature of the reaction chamber. The eutectic point of potassium perchlorate (m.p. 610°) with potassium chloride (m.p. 771°) is approximately 570° [24]; the other salts used were also high-melting, so that the mixture could not possibly have sintered or melted, and no signs of these phenomena have been detected in any of the experiments.

A consideration of the chemical nature of the catalysts employed and of the variation of their efficiency with the different forms of carbon, makes it possible to differentiate between the alternatives b) and c). With different halogenides of the same metal, no such regularity was observed as that found by Glasner and Weidenfeld[20] in the case of ammonium salts, which catalyse the thermal decomposition of potassium perchlorate increasingly with the atomic weight of the halogen. Thus, in the present case lithium bromide was a stronger catalyst than the chloride with carbon black and graphite, but a weaker one with nuchar; the potassium salts showed the sequence (in order of decreasing efficiency) chloride > bromide > iodide with carbon black; while with nuchar all three salts showed a slight (inhibitory) effect of similar magnitude; and only in the case of graphite could the sequence iodide > bromide > chloride be observed experimentally.

The extremely high melting point of all forms of carbon (above 3500°) appears to obviate the assumption that catalysts may influence the reactivity or mobility of the carbon atoms at the temperature of the experiments. (The experiments with graphite in the presence of potassium iodide may be an exception; the iodine or the potassium liberated in the course of the experiment may both react with graphite, penetrating between its layers and causing its disintegration[25-27].) The substance affected by the catalyst is, therefore, most probably the potassium perchlorate. In the case of those catalysts, which show strong activity with all forms of carbon, the effect may be due to a channelling or flux of oxygen atoms to the surface, aided by the attraction of the molecules of the catalyst[21]. This explanation could, however, be valid only for lithium chloride and bromide, both of which are active with all three forms of carbon as well as with the polymers studied, but it is difficult to understand why other halogenides should be active in some cases, but inactive or even inhibitory in others.

Incidentally, the very low activity of lithium and potassium carbonate and potassium orthophosphate tends to show that stable surface oxides play only an insignificant part, if any, in the reaction of carbon and polymers with potassium perchlorate, while in the catalytic oxidation by molecular oxygen the decomposition of surface oxides by basic substances has been postulated as the main catalytic effect[22,23,28-30].

The most logical explanation for the mode of action of the catalysts seems to be that given by c). Thus, if the catalyst lowers the energy level needed for the formation of a transition complex between the two reactants, the formation of this complex will still be dependent on the original physical and chemical properties of the different forms of carbon, and the same substance may catalyse the reaction of one form and inhibit the reaction of another form of carbon. The same reasoning can also be applied to a hypothesis according to which the catalysts act as oxygen carriers, by reacting with the perchlorate to form an (unstable) oxygenated intermediate XO_n^- (X denoting the anion of the catalyst). Part of the catalytic effect may be due to the intermediate diffusing at a higher rate than the perchlorate itself, either through the product layer or on the surface of the reactants (or both). Were this, however, the only or the main rate determining factor, one would have again to expect about equal or at least similar efficiency of the same catalyst with all forms of carbon. It seems, therefore, that the catalyst will have a marked accelerating action only if the intermediate XO_n^- reacts with the carbon much quicker than the perchlorate itself, and the overall reaction rate will vary considerably with the physical and chemical properties of the original surface of each type of carbon.

ACKNOWLEDGEMENT

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REFERENCES

1. Oza, T. M. and Shah, M. S., 1942, *J. Univ. Bombay*, **11**, 56.
2. Parry, R. W. and Comings, E. W., 1950, *Industr. Eng. Chem.*, **42**, 557.
3. Parry, R. W. et al., 1950, *ibid.*, **42**, 560.
4. Fieldner, A. C. and Brewer, R. E., 1946, *U.S. Bur. Mines Inform. Circ. No.* 7352.
5. Orleanskaya, G. L., 1950, *Izvest. Akad. Nauk. S.S.S.R., Otdel Tekh. Nauk.*, 1071. (*Chem. Abstr.*, **45**, 8739 (1951)).
6. Patai, S. and Hoffmann, E., 1950, *J. Amer. Chem. Soc.*, **72**, 5098.
7. Patai, S. and Hoffmann, E., 1951, *J. Appl. Chem.*, **2**, 8.
8. Patai, S., 1952, *Experientia*, **8**, 76.
9. Valyi, I., Jansen, A. G. and Mark, H., 1945, *J. Phys. Chem.*, **49**, 461.
10. Vogel, A. I., 1948, *Practical Org. Chemistry*, Longmans, Green and Co., p. 885.
11. Morrell, R. F., 1943, *Synthetic Resins*, 2nd Ed., Oxford Univ. Press, p. 112.
12. Marvin, G. S. and Woolaver, L. B., 1945, *Industr. Eng. Chem.*, **17**, 474.
13. Jander, W., 1927, *Z. Anorg. Chem.*, **163**, 1.
14. Tamman, G. and Mansuri, Q. A., 1923, *ibid.*, **126**, 119.
15. Taylor, H. S., 1925, *Proc. Roy. Soc.*, (A)**108**, 105.
16. Lewis, 1905, *Z. Physik. Chem.*, **52**, 310.
17. Otto, C. E. and Fry H. S., 1921, *J. Amer. Chem. Soc.*, **46**, 269.
18. Kendall, J. and Fuchs, F. J., 1921, *ibid.*, **43**, 2017.
19. Glasner, A. and Weindenfeld, L., 1951, *Bull. Res. Counc. of Israel*, **1**, No. 1—2, 118.
20. Glasner, A. and Weindenfeld, L., 1950, *Nature*, **166**, 109.
21. Glasner, A. and Simchen, A. E., 1951, *Bull. Soc. Chem.*, **18**, 233.
22. Patai, S., Hoffmann, E. and Rajbenbach, L., 1952, *J. Appl. Chem.*, **2**, 306.
23. Patai, S., Rajbenbach, L. and Hoffmann, E., *ibid.*, **2**, 311.
24. Benrath, A. and Braun, A., 1940, *Z. Anorg. Chem.*, **244**, 348.
25. Fredenhagen, K. and Cadenbach, G., *ibid.*, **158**, 249.
26. Fredenhagen, K. and Suck, H., *ibid.*, **178**, 353.
27. Riley, H. R., 1950, *J. Chim. Phys.*, **47**, 542.
28. Kroger, C. and Melhorn, G., 1938, *Brennstoff Chemie*, **19**, 157.
29. Blayden, E., Riley, H. R. and Shaw, F., 1943, *Fuel*, (London), **22**, 32, 64.
30. Wynne-Jones, W. F. K., Blayden, H. E. and Marsh, H. 1952, *Brennstoff Chemie*, **33**, 238.

SIMULTANEOUS AND HYDROGEN MICRO-ESTIMATION OF CARBON IN ORGANIC FLUORINE COMPOUNDS

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The simultaneous determination of carbon and hydrogen in fluorine-containing organic compounds is complicated by the fact that the water produced in the combustion reacts with the silicium tetrafluoride formed from the quartz of the combustion tube, so that the hydrogen of the sample appears partly in the form of hydrogen fluoride. In the present investigation an attempt was made to absorb the fluorine compounds produced in the combustion by lead dioxide, as it is employed in the combustion of nitrogenous organic compounds. This lead dioxide retains a constant amount of water at 180°, and it was the object of the present experiments to use the reaction of this water and of the lead dioxide with the silicium tetrafluoride formed for the fixation of the fluorine. It was expected that this method, if successful, would eventually permit the determination of carbon, hydrogen and fluorine in the same sample.

Only very recently methods for the determination of carbon and hydrogen in fluorine derivatives have been published. Belcher and Goulden[1] used silver for the absorption of fluorine (from hydrogen fluoride) and sodium fluoride for the absorption of silicium tetrafluoride, and Throckmorton and Hutton[2] employed for the purpose of absorbing silicium tetrafluoride a layer of magnesium oxide in addition to the usual lead dioxide-containing filling.

Preliminary experiments showed, indeed, that the combustion gases after passing a layer of lead dioxide at 180° were free of hydrogen fluoride. The estimation of carbon and hydrogen in a quartz tube containing a layer of lead dioxide gave satisfactory figures for carbon, but the values for hydrogen were too high, however, in a fully reproducible manner. This observation led us to apply a correction to the results for hydrogen, as obtained from the increase of the weight of the water absorption tube. This correction was based on the assumption that the following reactions take place in the lead dioxide layer ($Me = Pb^{II}$ or $\frac{1}{2}Pb^{IV}$):

$$1)\quad SiF_4 + 2H_2O = SiO_2 + 4HF$$
$$2)\quad 4HF + 2MeO = 2MeF_2 + 2H_2O$$
$$3)\quad 2MeF_2 + 2SiF_4 = 2MeSiF_6$$

or:

$$2)\quad 4HF + 2SiF_4 = 2H_2SiF_6$$
$$3)\quad 2MeO + 2H_2SiF_6 = 2MeSiF_6 + 2H_2O$$

In both cases, two molecules of water contained in the lead dioxide layer react with the oncoming silicium tetrafluoride, forming four molecules of hydrogen fluoride which in turn give a silicofluoride of lead and liberate two molecules of water which passes into the hydrogen absorption tube. In the latter therefore, one molecule of water is found for each six fluorine atoms in the sample. If the percentage of fluorine in the sample is known, the hydrogen value obtained has to be reduced by 1/57 of the fluorine percentage of the sample; if the analysis is to confirm an assumed formula, it is recommended to correct the error in the result by the following formula:

$$H = H_R - H_R\,(N_F / 3) / (N_H + N_F / 3)$$

$$H = H_R \cdot 3N_H / (3N_H + N_F)$$

where H = corrected H value, H_R = found H value, N_H = assumed number of hydrogen atoms in the molecule, and N_F = assumed number of fluorine atoms in the molecule.

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The experimental results are summarized in Table I. It can be seen that for substances with low F:H ratio the correction formula is not necessary.

The results obtained with compounds of comparatively high fluorine content, like trifluoroacetic acid, heptafluorobutyric acid and an ether $C_6F_{12}O$ justify the proposed procedure. In the case of trifluoroacetic acid, for instance, the observed hydrogen value of 1.84% is reduced by the formula to 0.92 (theor: 0.88), in that of heptafluorobutyric acid that of 1.92% to 0.57% (theor: 0.47%). In the case of the compound $C_6F_{12}O$ the deviation from the result is just outside the error of the method; it may thus be necessary to increase the lead dioxide layer for compounds of very high fluorine content.

Table I shows also that organic fluorine compounds containing nitrogen (as amino or nitro groups) analyse satisfactorily for carbon and hydrogen. It is easy to carry out with this method serial analyses, as the point at which the lead dioxide layer is spent can be recognised without difficulty: the quartz tube turns opaque just after the lead dioxide layer and a steep rise in the hydrogen values is observed. Compounds of high F content and low H do not appear to represent any difficulties. It is noteworthy that even compounds which contain less hydrogen than fluorine atoms give correct results, and the question arises, what happens in the combustion of such substances in a current of oxygen. The fluorine does not combine with carbon, as otherwise the carbon value will show deficiencies — which have not been observed — and one will have to assume that silicium tetrafluoride is formed in the combustion zone. This assumption has also been made by Teston and McKenna[3] in their method for the analysis of fluorocarbons, but the actual mechanism of the combustion process under these conditions will require further study.

Another point to be explored is the mechanism of the reaction that takes place in the lead dioxide layer. The knowledge of this mechanism may make it possible to determine simultaneously carbon, hydrogen and fluorine, using a weighed amount of lead dioxide in a detachable container. In this case, of course, the sample should not contain nitrogen as the lead dioxide also absorbs nitrogen oxides. Research in this direction is being carried out at present.

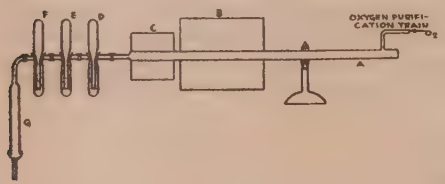

Figure 1
A—combustion tube; B—primary furnace, 1000°; C—secondary furnace, 180°, D—water absorption tube; E—carbon dioxide absorption tube; F—weighing control; G—safety tube.

Apparatus and Procedure

Oxygen purification train: Conventional setup, as described by Niederl and Niederl[4].

Combustion tube: Transparent quartz, about 60 cm long, 9 mm bore with sidearm and exit tube, both 5 mm outer diameter.

Absorption train: 3 Friedrich absorption tubes, one for water, one for carbon dioxide and one as weighing control; one safety tube.

Primary Furnace: A Fischer micro-combustion furnace of 17 cm length adapted for temperatures up to 1000°. The temperature is measured by a Chromel-Alumel couple.

Secondary furnace: Electrically heated, kept at 180° (standard thermometer).

Both furnaces have a bore of 13 mm to take the combustion tube and allowing space for the thermocouple in the primary furnace. A movable copper arm protrudes from the secondary furnace resting on the entry tube of the water absorption vessel.

Filling of the combustion tube: A standard platinum star of 5 cm length protrudes from inside the primary furnace towards the inlet of the oxygen stream. Inside the furnace, it is followed by four layers of crushed quartz alternating with four rolls of platinum wire, the last one extending into the secondary furnace. Then follow a thin layer of asbestos wool, a layer of lead dioxide prepared and purified according to Niederl and Niederl[4], a choking plug of asbestos wool and finally a roll of silver wool.

Filling of absorption tubes: The water absorption tube is filled with Anhydrone, the carbon dioxide absorption tube and the control tube half with Ascarite and half with Anhydrone. The safety tube is filled with granulated sodium hydroxide and is connected to the usual Mariotte bottle.

Connections: Glass to glass, with thick-walled, impregnated, seamless rubber tubing.

The procedure follows exactly that of the classical micro-combustion analysis for carbon and hydrogen[4], except for the temperature in the primary furnace which is being kept at 1000°. Owing to the higher temperature in the combustion zone and to the tendency of some fluorine compounds to "back-firing", the burner has to be moved more slowly than it is usual during the combustion.

Weight of sample: about 5 mg.

TABLE 1

Compound	Formula	Theoretical		Found	H-values, reduced according to correction formula *a*		Found, average	
		C(%)	H(%)	C(%)	H(%)	H(%)	C(%)	H(%)
4-Fluoro-biphenyl *b*	$C_{12}H_9F$	83.7	5.2	83.8	5.3	5.1		
				83.4	5.4	5.2		
				83.9	5.4	5.2		
				83.5	6.0	5.7		
				83.4	5.3	5.1		
				83.9	5.6	5.4	83.7	5.3
4,4'-Difluorobianthrone *c*	$C_{28}H_{16}O_2F_2$	79.6	3.8	80.2	3.8	3.7		
				79.8	3.5	3.4	80.0	3.6
2-Nitro-5-fluorobenzoic acid *d*	$C_7H_4O_4F$	45.4	2.2	45.4	2.8	2.6		
				45.8	2.8	2.6	45.6	2.6
(1,1-Diphenyl-2,2,2-trifluoro-ethyl) acetate *e*	$C_{16}H_{13}F_3O_2$	65.3	4.5	65.6	4.7	4.4	65.6	4.3
				65.7	4.4	4.1		
2-Nitro-5-fluorotoluene *f*	$C_7H_6O_2NF$	54.2	3.9	54.4	4.1	3.9		
2-Nitro-4-fluorotoluene *g*	$C_7H_6O_2NF$	54.2	3.9	54.8	3.9	3.7		
				54.8	4.3	4.1	54.8	3.9
3-Fluoroacetanilide *h*	C_8H_8ONF	62.7	5.2	63.1	5.5	5.3		
				63.1	5.4	5.2	63.1	5.25
1.1-Di-(*p*-fluorophenyl)-2-nitro-ethane *i*	$C_{14}H_{11}O_2NF_2$	63.9	4.2	63.6	4.2	4.0	63.6	4.1
				63.6	4.4	4.2		
Trifluoroacetic acid *k*	$C_2HO_2F_3$	21.1	0.88	21.2	1.62	0.81		
				21.3	1.68	0.84		
				21.2	1.84	0.92		
				20.8	2.24	1.12		
				20.9	1.82	0.91	21.1	0.92
Heptafluorobutyric acid *k*	$C_4HO_2F_7$	22.45	0.47	22.04	1.92	0.58		
Ether *k*	$C_6F_{12}O$	22.8	0.0	22.3	1.69	0.4		
				22.9	1.65	0.4	22.6	0.4

$a - H = H_R \cdot 3 N_H / (3 N_H + N_F)$

b — Prepared according to Schiemann and Roselius, 1929. *Ber.*, **62**, 1805; Roe and Fleishman, 1947, *J. Amer. Chem. Soc.*, **69**, 524, M.p. 75°

c — Bergmann and Loewenthal, unpublished results. Fluorine analysis according to Clark, 1951, *Anal. Chem.*, **23**, 659, gave F, 8.9% (theor: 9.0%).

d — Bergmann and Bendas, unpublished results. M.p. 134.5°

e — Kaluszyner, unpublished results.

f — Schiemann, 1929, *Ber.*, **62**, 1802. M.p. 28°.

g — Slothouwer, 1914, *Chem. Centralbl.*, **2**, 1431. B.p. 51—52° (0.7 mm).

h — Bergmann and Bentov, 1953, *Bull. Res. Counc. of Israel*, **2**, 280. M.p. 78.2°. N,calcd.: 9.2; N, found: 9.2.

i — F. Bergmann, unpublished results. N, calcd.: 5.3 N, found: 5.3.

k — Commercial preparations.

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REFERENCES

1. Belcher and Gouden, 1951, *Mikrochemie*, **36/37**, 679.
2. Throckmorton and Hutton, 1952, *Anal. Chem.*, **24**, 2003.
3. Teston and McKennan, 1947, *Anal. Chem.*, **19**, 193.
4. Niederl and Niederl, 1948, *Micromethods of Quantitative Organic Analysis*, 2nd ed., New York.

ON THE ADSORBTION OF ACTIVE GASES FROM STREAMING AIR

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INTRODUCTION

The selective adsorption from a gaseous mixture passing through a bed of a suitable adsorbent is of considerable importance in research and industry. This work deals with the adsorption of noxious gases streaming through a bed of activated charcoal. It is restricted to the processes which occur under the special conditions of the gas mask.

THEORETICAL

Mathematically, we may describe a fllow of air + noxious gas through an actived charcoal bed (or some other adsorbent) in the following manner[1]: From conservation of mass it follows that at each cross section the quantity of entering gas = the quantity adsorbed + the outgoing mass of the noxious gas (Figure 1):*

$$(c + dc)vdt + Adz(\partial n/\partial t)\,dt = cvdt \qquad (1)$$

and hence:

$$dc = -(A/v)(\partial n/\partial t)\,dz \qquad (2)$$

If we assume one-dimensional flow, c will depend on z and t only, and thus:

$$dc = (\partial c/\partial z)\,dz + (\partial c/\partial t)\,dt \qquad (3)$$

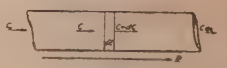

Figure 1
Distribution of gas concentration in adsorbing bed

Finally, using for the volumetric rate of flow the expression $v = \alpha uA$:

$$1/\alpha(\partial n/\partial t) = \partial c/\partial t + u(\partial c/\partial z) \qquad (4)$$

Regarding the mechanism of removal of the noxious gas, the following steps may be assumed:

(a) Molecular diffusion from the air to the outer surface of the charcoal granule and thence into and along its inner pores.

(b) Adsorption on the surface area.

(c) Chemical reactions between the adsorbed gas and the charcoal or adsorbed atmospheric water or some metallic impregnant which is usually deposited on the adsorbent.

Consequently, the local rate of adsorption per unit volume will vary with the nature of the adsorbent and the adsorbate ,the geometric configuration of the bed, the local concentration of the noxious gas, the quantity previously adsorbed, the rate of flow of the gaseous mixture and the temperature.

Equation (4) can be solved if $\partial n/\partial t$ is assumed to be governed by one rate-controlling step only. Using this simplification and also assuming linear adsorption isotherms, some mathematical solutions are obtained [2,3,4]. However, none of these solutions show satisfactory agreement with experiment.

The problem may be approached from a somewhat different angle and can be dealt with by devising some semi-empirical correlations between such variables as the "life time" of the adsorbing bed, its thickness, the initial concentration of the gas, etc. If one plots the time elapsed till a certain concen-

* For the nomenclature see end of paper.

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tration of the effluent gas is reached as a function of z, it is possible to distinguish between two main types of experimental curves (Figure 2). Type *A* represents the case of most of the organic gases and dry activated charcoal while *B* corresponds to "cumulative life time (t_c)" tests and, usually, to the processes carried out with wet gases and charcoal. These curves clearly show the existence of a critical value of z, below which the bed's life drops to zero and which obviously determines its adsorptive efficiency. Using the law of conservation of mass and disregarding the negligible amount of gas escaping at break time, it follows that: The mass of the entering gas = the mass of the adsorbed gas. Assuming immediate adsorption to begin only after the critical depth I is passed, one gets[5]:

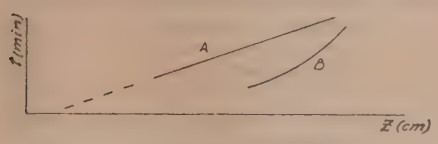

Figure 2
Life time—thickness curves

$$t_b c_o v = N_o A(z - I) \tag{5}$$

The critical depth itself depends on characteristic parameters of the gas and the charcoal such as the Reynolds number, the Schmidt number, the ratio between the in- and outgoing concentrations, etc.[6,7] Moreover, for dry gases it was found to obey the simple equation:

$$I = const.u^k \quad \text{or:} \quad I = g(v_e/A_b)^k \log c_o/c_b \tag{6}$$

which gives as a convenient working formula:

$$t_b = (N_o A/c_o v)\,[z - g(v_e/A_b)^k \log c_o/c_b]. \tag{7}$$

Equation (7) was tested[8] with several noxious gases and was found to be in fair agreement with experiment.

The theoretical treatment stresses the importance of the following parameters: The chemical nature of the noxious gas; its flow rate; its initial concentration; the geometric configuration and the inner arrangement of the adsorbing granules in the bed (which is connected with problems of heat of adsorption or chemical reaction and its dissipation) and the temperature. Hence it is usual to carry out the efficiency tests of a certain adsorbent under the following conditions[9,10,11,12]:

(a) The bed is tested with several typical gases.

(b) The test is performed with the actual adsorbing configuration — in the present case the canister of the gas mask itself.

(c) The mixture of air + noxious gas flows at a rhythmic rate simulating the human respiration cycle under heavy physical strain (an important requirement for this work).

(d) The gas mask is examined at high atmospheric humidities, which appear to influence unfavourably the adsorptive efficiency,

The rate of flow, or the rate of breathing, obeys an equation of the type:

$$v = A_l \sin \omega t \tag{8}$$

A few absolute values of v are given in Table I.[13]

TABLE I

Degree of exertion	Maximal instantaneous rate of flow (lpm)	Average rate (lpm)	Inhalatory part of the total cycle %	Number of respirations per minute
Heavy (can be sustained for 30' only)	126	44	51	29
Maximal (can be sustained for 10' only)	176	63	51	29

METHOD FOR TESTING THE EFFICIENCY OF ADSORPTION

Applying the principle outlined in the paper by Fieldner et al.[14] a somewhat modified testing apparatus was constructed. Essentially, a mixture of air + noxious gas is continuously passed through a gas mask and a part of it is sucked (at predetermined times) through appropriate absorption bottles. The gas takes part in a quantitative chemical reaction as a result of which it is possible to determine its effluent concentration as a function of time. Actually, in the older method a known relative humidity (50%) and a fixed flow rate (32 lpm) were already employed. Nevertheless, on account of modern requirements, the physical working conditions were altered to a certain degree.

For the design of the apparatus three points were taken into account particularly:

(a) A rhythmic type of flow at a suitable rate had to be obtained.

(b) A convenient device for air humidification had to be constructed.

(c) The analytical sensitivity of the reaction had to be increased. Accordingly, the apparatus shown in Figure 3 and 4 was built.

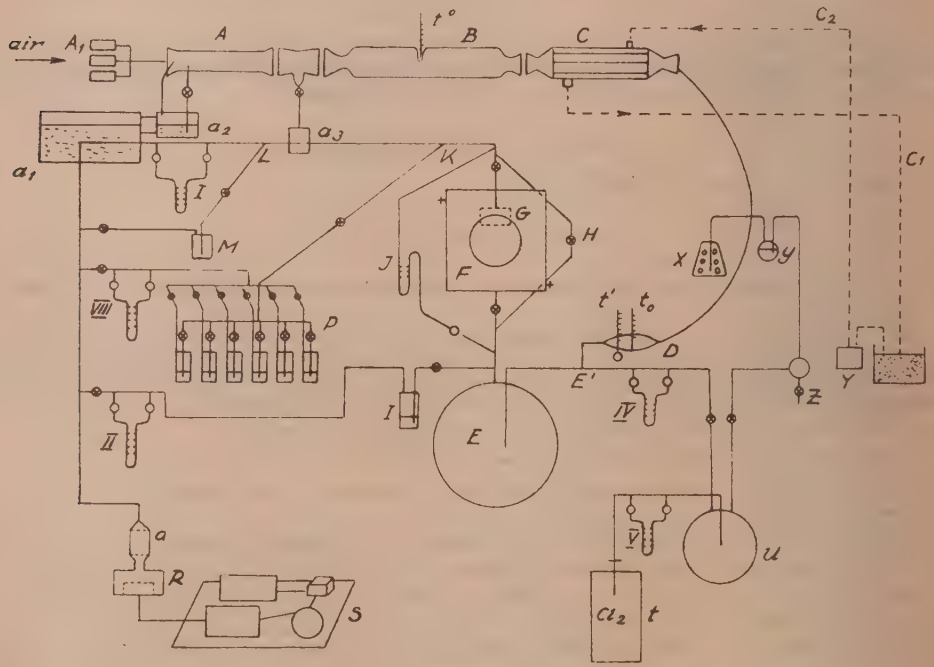

Figure 3
Diagram of apparatus

The apparatus is divided into a humidification branch, a gas supply line, a mixer, an analyzer and a pump.

Humidification branch: A_1— an electrically heated air dryer, *A*—a venturi tube with injection attachment. *B*—an electrically heated evaporator. *C*—a water cooler of large surface area (C_1, C_2—conducting pipes, *Y*—liquid centrifugal pump). *D*—a "wet and dry bulb thermometer" for measuring humidity.

Gas supply line: t—a cylinder of Cl_2. *V*—flowmeter. *u*—a reservoir (5000 ml) for reducing the fluctuations of the gas density. *IV*—flowmeter. *x*,*y*,*z*—safety device for cases of overpressure in the reservoir. The *mixer E* is a 12 litre flask and the *canister holder* consists of a metallic box *F* the ends of which are attached to a manometer with a $CaCl_2$ solution ($\varrho^{25°} = 1.20$ g/cm^3). (Behind the box there is a by-pass *H* the resistance of which can be equalled to that of the canister with the aid of a stopcock.).

Analyzer: *P*—six absorption bottles. *VIII*—flowmeter. *M*—absorption bottle for the qualitative indication of the "break time" t_b. *I*—bottle for the quantitative determination of the influent concentration, with an additional flowmeter. The *suction line* has a reciprocating pump *S*, an adsorber *R,Q* (*R*—gas mask canister. *Q*— container filled with a suitable adsorbent) for its protection and a preceding flowmeter.

Figure 4
Photograph of apparatus

TESTING PROCEDURE

After starting the pump, the air commences to flow through A_1, becomes dry and reaches the venturi tube, into the throat of which it draws a calculated amount of water to be atomized. (This quantity may be regulated by a stopcock placed between a_2 and *A*). The resulting drops of water are carried to *B* (heated to a temperature of 60°C), where they evaporate completely. In *C* the hot and humidified air cools down to room temperature, partly passes through the hygrometer *D* and joins a secondary flow of gas (Cl_2) at *E'*. The latter, regulated previously while passing through *u-z-y* and the adsorber *x* (granules of $CaO.x\ H_2O$) is also sucked into the main line at zero time. The combined streams mix in the flask *E* and continue to flow through the canister *G*. Thence, the mixture passes flowmeter *I*, reaches the reciprocating pump through *R,Q* and escapes into the atmosphere.

For analysis, a part of the outgoing flow is turned initially to *M* where it bubbles through an aqueous solution of potassium iodide+starch. After some time t_b, this solution acquires a blue tinge, an appropriate indication for commencing the quantitative analysis. The analysis is performed by switching the flow to one of the *P* bottles, bubbling it through an aqueous solution of sodium thiosulphate+potassium iodide and starch and measuring the time elapsed till the appearance of a blue colour. The effluent quantity of Cl_2 is determined by the reactions:

$$(9)\quad Cl_2 + 2I^- \longrightarrow I_2 + 2Cl$$

$$(10)\quad I_2 + 2S_2O_3^{--} \longrightarrow 2I + S_4O_6^{--}$$

while the volume of the mixture is given by the product of elapsed time and rate of flow. Thus, the concentration of the Cl_2 can be evaluated at any desired time. Similarly, as a check of the flowmetric measurements, it is possible to determine the initial concentrstion of the gas with the aid of *I* and flowmeter *II*.

DETAILED DESCRIPTION OF APPARATUS

Pump: This is more or less a copy of the instrument described in the paper by Thomas[15] (Figure 5). The air is drawn from the system through the valve *A* and escapes through *B* at a rate expressed by the equation:

$$d\Phi/p_1 = 182.9[\sin\Theta + R_1 \sin\Theta \cos\Theta \Big/ \sqrt{L^2 - (R_1 \sin\Theta)^2}] \qquad (11)$$

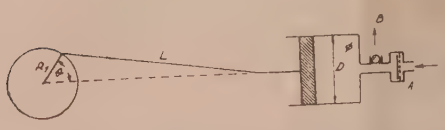

Figure 5 Breather Pump

With sufficient accuracy the second term in the brackets may be neglected and a purely sinusoidal flow be assumed[15].

The measurement of the pulsating flow encountered here presents a difficult problem[16,17,18]. It can be shown, however[15], that, for the instantaneous maximal value, the conventional methods of measurement may be used with a fair approximation. The rate of flow at any place in the system is measured at its maximum value by a simple flowmeter calibrated previously. Assuming a constant frequency throughout the system, the average rate is calculated by:

$$\bar{v} = \left\{A_i \int_0^{\pi} [\sin\Theta + R_1 \sin\Theta\cos\Theta / \sqrt{L^2 - (R_1 \sin\Theta)^2}]\, dt\right\} \Big/ T \sim \left\{A_i \int_0^{\pi} \sin\Theta dt\right\} \Big/ T = A_i/\pi \qquad (12)$$

The actual values reached are 160 lpm maximum rate and 51 lpm average.

Analyzer: This branch consists of six absorption bottles and a flowmeter (Figures 6, 7). For the

Figure 6
Absorption Bottle

Figure 7
Photograph of Analyzer

determination of Cl_2* the aforementioned method is used. This method is convenient, rapid and sensitive enough at the low concentrations encountered in hygienical and physiological research. In addition, the surplus of thiosulphate present during the analysis prevents any entrainment of the liberated iodine. The minimal concentration which still produces an observable blue colour may be calculated as follows: At room temperature and with an iodide concentration >0.001 N, the sensitivity of the starch-iodine reaction was found to be $1\text{-}2.10^{-5}$ N iodine (in agreement with Kolthoff and Sandell[19]). Consequently one needs at most 0.021 mgCl_2 in order to produce a blue tinge in 30 cm^3 of solution. Thus bubbling the gas through the liquid for one minute** at $\bar{v}$:

$$c_{Cl_2} = (m_1 + 0.021) / \bar{v} \text{ mg/l} \tag{13}$$

whence the minimal concentration is given by:

$$c_{min} = 0.021 / \bar{v} \tag{14}$$

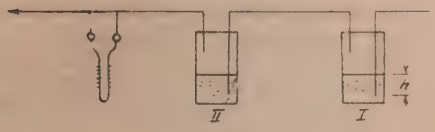

Figure 8

The last value is obviously inversely proportional to the rate of flow. However, while tending to increase the latter, one has to make sure that the Cl_2 is absorbed completely. This was done by passing the mixture of air and Cl_2 through M, two absorption bottles and a suitable flowmeter at different flow rates and heights of liquid absorbent (Figure 8). The first bottle, geometrically similar to one of the P bottles, contained a solution of thiosulphate, iodide and starch, and the second, starch and iodide only. The results are summarized in Table II.

TABLE II

$\bar{v}$ (lpm)	Height of liquid (cm)	Results
2.0	3	I become blue before II
2.2	3	"
3.0	3	"
≃1.4	3.5	"
≃1.4	2	"
≃1.4	1.8***	"
≃1.4	1.6	"
≃1.4	1.0	II becomes blue before I
≃1.4	0.5	

The table shows that at the working conditions ($\bar{v} =$ 1.8 lpm) the absorption is satisfactory. Thus the minimal observable concentration becomes 0.01 mgCl_2/l; by comparison the "insupportable concentration" for Cl_2 is[20,21] 0.1 mg/l.

Gas supply line: The flow within the reservoir u is regulated in such a way that the total amount of Cl_2 outgoing during the half period of suction is equal to the amount entering during the whole cycle (Figure 9.) Hence:

$$Ai \int_0^{\pi} \sin \Theta \, dt = \bar{v}_v T \tag{15}$$

A simple calculation shows that the fluctuations of the gas density in the reservoir are small and can be neglected.

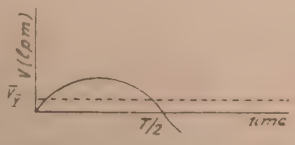

Figure 9
Average gas supply during a complete breathing cycle

Air humidification branch: This branch is composed of a cooler, an evaporator, a venturi tube and an air dryer.

(a) *Cooler:* Taking into account the resistance to flow and aiming at compactness, a type of cooler was chosen that consisted of ten

* An additional determination of HCl was carried out after the completion of the chlorine analysis. However, since the pH of the solutions remained unchanged, the determinations of HCl were discontinued.

** By comparison, the complete canister test lasts 30—60 minutes.

*** The initial concentration of Cl_2 was 0.21 mg/l.

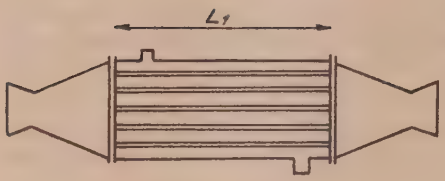

Figure 10 Cooler

straight tubes connected in parallel (Figure 10). Assuming an appropriate temperature of the incoming air, the outgoing air and the cooling surface*, the effective length of these tubes was calculated by the following formula[22]:

$$(L_1 / D_i') (\triangle \tau_m / \tau_1 - \tau_2) = 4.52 (D_i' G')^{0.2} \qquad (16)$$

Choosing $\tau_1 = 140°F$, $\tau_2 = 77°F$ and $\tau_o = 32°F$ and assuming a steady flow of 2.78 lps, which constituted an unfavorable exaggeration, this length was found to be 1 ft. In order to be on the safe side the tube length was finally increased to 40 cm.

(b) *Evaporator and venturi tube:* These two parts are closely connected since the rate of flow determines both the diameter of the drops formed at A and the time of their remaining within the evaporator. For various technical reasons an evaporator was designed, the dimensions of which are shown (Figure 11). Assuming zero relative velocity between the drops entering the evaporator and the air and very rapid heating of this mixture to a constant temperature (60°C) throughout the evaporator, the present problem reduces to the case of the evaporation of drops into air under thermal equilibrium.

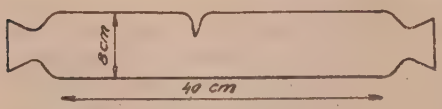

Figure 11 — Evaporator

The instaneous rate of evaporation is then expressed by the equation[23]:

$$-dm_2 / dt = (D_w P / R\tau r) 4\pi r^2 (y_i - y) \qquad (17)$$

which gives, after integration:

$$t_o = r_o^2 R\tau / 2D_w.P (y_i - y) \qquad (18)$$

Putting t_o=0.72 sec (corresponding to the maximum flow rate of 2.78 lpm**), y=0.027*** and assuming y_i= 1, one gets $d_o = 78\mu$ as the maximum drop size which evaporates completely under the assumed conditions. Different values of d_o were calculated for various flow rates and are presented in Table III and Figure 12.

The average diameter of the drops formed by injecting water into the throat of the venturi tube was calculated according to the well known formula of Nukiyama and Tanasawa[24].

$$****d_m = (585 / u_1) \sqrt{\sigma / \varrho_1} + 597 (\mu / \sqrt{\sigma \varrho_1})^{0.45} (1000 Q_L / Q_G)^{1.5} \qquad (19)$$

The validity of this equation is limited to subsonic gas velocities and to a liquid of density 0.7—1.2 g/cm^3, of viscosity 0.003—0.5 poise and of surface tension 13—73 dyne/cm. Putting into (19) the numerical values corresponding to 298°K and 100% relative humidity, one gets:

$$d_m = 4961 / u_1 + 0.094 \qquad (20)$$

Actually, the sprayed drops form a spectrum of sizes[26] of a certain distribution but this fact has not been taken into account. Different values of d_m for various flow rates are given in Table III and Figure 12.

It is clearly seen that, within the range of validity of the assumed equations, there exists a critical velocity below which the formed drop does not evaporate completely and, therefore, the spraying must be performed at higher velocities. The water can be prevented from being injected into the venturi tube by lowering its reservoir a_2 (Figure 3) to a certain depth below the throat. This depth is determined by the pressure difference between the entry and the throat which just suffices to draw the liquid

* Which is, approximately, the temperature of the cooling water.
** On the assumption of ϱ = const.
*** Which corresponds to the unfavourable case of 100% relative humidity.

**** The diameter $d_m = X_m$ ("Sauter's mean diameter") is defined by[25]: $X_m = \int_{x_o}^{xp} x^3 (dn/dx)\, dx \,/\, \int_{x_o}^{xp} x^2 (dn/dx)\, dx$

where n is the number of drops having a diameter between X and $X+dX$.

TABLE III

u_1 (m/sec)	Time of remaining in evaporator (sec)	d_m (μ)	d_0 (μ)
250	0.72	19.8	78
200	0.9	24.8	85
125	1.44	39.6	110
100	1.8	49.6	123
50	3.6	99	171
25	7.2	198	245

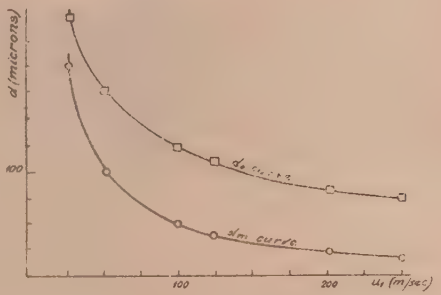

Figure 12
d_0 and d_m *vs.* rate of flow in venturi throat

into the gas stream. Accordingly, the venturi tube and reservoir were designed as in Figure 13. The Ψ^* at the throat of the venturi tube, corresponding to the maximal flow rate of 2.78 lps, has been fixed at 0.95. By computation, on the assumption of one-dimensional and isentropic flow, one gets at the throat: $D_1 = 0.432$ cm and $u_1 = 250$ m/sec. The above mentioned critical velocity has been fixed at 50 m/sec, whereupon the diameters of the drops have been limited to the range of about 20—100/μ (*cf.* Table III). The depth H required for achieving this result has been calculated to be approximately 15 cm.

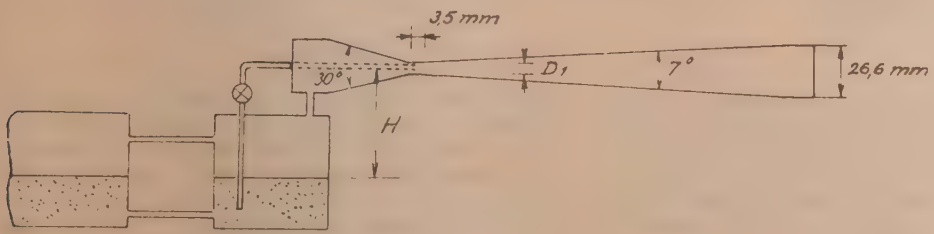

Figure 13
Venturi tube and water reservoir

The duration of the injection time may be computed as follows: Putting into equation (8) the value corresponding to the critical velocity at the throat (50 m/sec), one gets:

$$\sin 2\pi\nu t = 0.2 \tag{21}$$

whence the corresponding time results as 0.05 sec. It follows then that 87% of every half-period is subjected to injection (Figure 14).

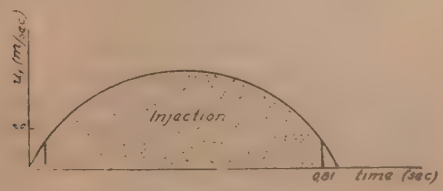

Figure 14
Fraction of inhalatory cycle subjected to injection

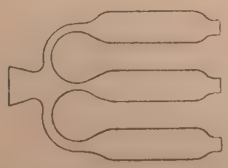

Figure 15
Air dryer

* $\Psi = u\varrho / u^*\varrho^*$

(*c*) *Air dryer:* This part consists of 3 cylinders joined together which are filled with $CaCl_2$ granules. Its dimensions were determined by consideration of resistance to flow and final size (Figure 15). In the range of relative humidities investigated (50—100%) the dryer proved to be superfluous and therefore, for the time being, it was disconnected. It is worthwhile mentioning, though, that the employed humidities constitute rather severe testing conditions[12].

(*d*) *Experiments with the humidification branch:* In the first experiment, in spite of the injection of relatively enormous quantities of water into *A*, the relative humidity rose only slightly while most of the injected liquid accumulated on the bottom of the evaporated *B*. While examining the venturi tube in operation separately it was found that the drops, formed by the radial injection into the throat, impinged (Figure 16) on the opposite wall, coalesced there and flowed as a thin liquid stream into the evaporator. On the other hand, when using axial injection, a fine spray was obtained with most of the drops being carried over into *B* without impaction.

Figure 16
Trajectory of a water drop formed by radial injection

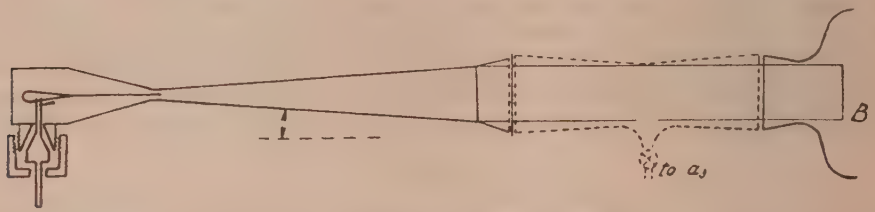

Figure 17 — Injector, venturi tube and sink

The injector finally adopted is shown in Figure 17. The efficiency of spraying, i.e. the fraction of the injected water which leaves the venturi tube in the form of fine drops, was found to be 60%. The undispersed water which deposited on the wall of the venturi tube was drained through the sink a_3 placed between *A* and *B*. The line was tilted to ensure proper drainage. In order to test the efficiency of evaporation, water was injected into the venturi tube and the air + water mixture passed through the unheated evaporator. A marked Tyndall effect was observed at the outlet of *B* which disappeared immediately after heating the evaporator to the operating temperature.

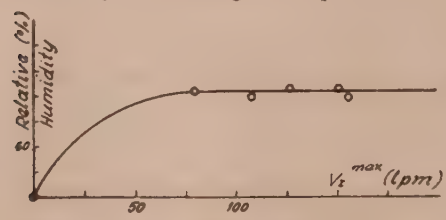

Figure 18 — Relative humidity readings *vs.* rate of flow

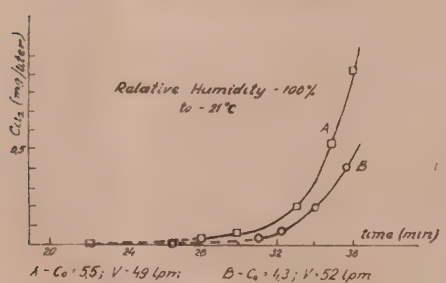

Figure 19 — Experimental results

The humidification branch enables to obtain relative humidities ranging from the atmospheric value up to 100% which stay constant during the canister testing period.

(*e*) *Hygrometer D:* At low rates of flow the "wet and dry bulb thermometer" readings are known to depend on *u* and the true values are reached only asymptotically. Constant readings were observed within the range of $v_t^{max} = 74$—155 lpm (Figure 18) which is sufficient for the determination of the adsorptive efficiency as a function of *u*.

EXPERIMENTAL RESULTS

The results brought in Figure 19 may serve as examples for typical canister tests. The shape of these curves is seen to correspond rather closely to that described in the literature[2].

ACKNOWLEDGMENT

The author expresses his thanks to Mr. M. D. Bitron for his fruitful suggestions and helpful criticism in connection with this work.

NOMENCLATURE

A — cross section of adsorbing bed
A_b — cross section of outlet valve in gas mask canister
A_i — amplitude of rhythmic flow rate
c — concentration of noxious gas over adsorbent
c_o — influent concentration of noxious gas
c_{Cl_2} — effluent concentration of noxious gas
c_b — "break concentration" of noxious gas
D — diameter of piston (= 5.127″)
D_1 — diameter of throat
D_i' — inner diameter of tubes (inches)
D_w — diffusion coefficient of liquid molecules
d — diameter of liquid drop
d_o — initial diameter of liquid drop
G' — mass rate of flow (lb/sec-ft^2)
g — a constant
K — a constant
L — length of connecting rod (= 11.375″)
L_1 — length of tubes (feet)
m_1 — quantity of chlorine equivalent to appropriate amount of $Na_2S_2O_3$
m_2 — mass of water droplet
N_o — full adsorptive capacity per unit volume of adsorbent
n — concentration of noxious gas on adsorbent per unit volume
p — total pressure
Q_L/Q_G — ratio between volumes of dispersed liquid and atomizing gas.
R — universal gas constant
R_1 — radius of wheel (= 2.3125″)
r — radius of liquid droplet
r_o — initial radius of liquid droplet
t — time
t_o — time of complete evaporation
t_b — "break time"
t_c — "cumulative break time", after which the total quantity of effluent gas reaches a certain value
T — the period
u — linear velocity of air, or of air + gas mixture (cm/sec)
u_1 — linear velocity of air (m/sec)
u^* — linear flow rate, equal to the velocity of sound on the same streamline
v — volumetric flow rate (v_i max—maximal, * $\overline{v}_i$ — average)
v_e — steady flow rate equivalent to the rhythmic velocity
y_i, y — mole fractions of evaporating liquid in the gas, at the interface and at infinite distance, respectively
z — coordinate of length in adsorbing bed
α — porosity of adsorbing bed (= ratio of free to total volume)
ϱ — density of air
ϱ^* — density corresponding to u^*
ϱ_1 — density of liquid injected into venturi tube (g/cm^3)
σ — surface tension of liquid injected into venturi tube (dyne/cm)
μ_1 — viscosity of liquid injected into tube (poise)
τ — temperature
$\triangle \tau_m = \{(\tau_1 - \tau_o) - (\tau_2 - \tau_o)\} / \ln \{(\tau_1 - \tau_o)/(\tau_2 - \tau_o)\}$
τ_1 — temperature of incoming air
τ_2 — temperature of outgoing air
τ_o — temperature of cooling surface

* through flowmeter i.

Φ — volume enclosed within the piston
ν — frequency of rhythmic flow within the apparatus
$\omega = 2\pi\nu$
$\Theta = 2\pi\nu t$ = phase

REFERENCES

1. KLOTZ, I. M., 1946, *The Adsorption Wave*, Handbook on Aerosols. Chap. 1, A. E. C. of U.S.A. (also *Chem. Rev.*,, 39, 241.)
2. BOHART, G. S. and ADAMS, E. Q., 1920, *J.A.C.S.*, 42, 523.
3. DANBY, C. J., DAVOUD, J. G., EVERETT, D. H., HINSHELWOOD, C. N. and LODGE, R. M., *The Physical Chemistry of the Respirator*, Oxford University.
4. DREW, T. B., SPOONER, F. M. and DOUGLAS, J., Nov. 17, 1944, *NDRC* 10-5-48 *Div* 10-202-.157-M8.
5. MECKLENBURG, W., 1925, Z. *Elektrochemie* 31, 488 1930, *Kolloid. Z.*, 52, 88.
6. HURT, D. H., 1943, *Ind. Eng. Chem.*, 35, 522.
7. KLOTZ, I. M., Jun 13, 1944, Factors in Canister Design and Tube Testing—Critical Bed Depth and the Nature of Gas Flow Through Charcoal, *OSRD Rep.* 3774.
8. SHORT, O. A., and PEARCE, F. G., Nov. 25, 1944, *MIT-MR* 114.
9. *Science in World War II, Chemistry*, Little, Brown and Co., 1948, Chap. XXIII, 304.
10. *ibid.* 303 (also reference 17).
11. *ibid.* 303.
12. *ibid.* 296.
13. HORMAIS, S., Apr. 1951, *Arm. Forces Chem. Journal*, 30.
14. FIELDNER, A. C., OBERFELL, G. G., TEAGUE, M. C. and LAWRENCE, J. N., 1919, *Ind. Eng. Chem.*, 11, 519.
15. THOMAS, J. W., Oct. 1948, Air Flow Characteristics of the Breather Pump, *Arm. Forces Chem. Journal*, 44.
16. DESCHERE, A. R., 1952, *Trans. of ASME*, 74, 919.
17. HALL, N. A., *ibid.* 925.
18. BAIRD, R. C., and BECHTHOLD, I. C., *ibid*, 1381.
19. KOLTHOFF and SANDELL, 1950, *Text Book of Quantitative Inorganic Chemistry*, revised ed., 618.
20. SARTORI, *The War Gases*, J. and L. Churchill ed., 37.
21. JACOBS, M. B., 1944, *The Analytical Chemistry of Industrial Poisons, Hazards and Solvents*, Interscience Pub. Inc., New York.
22. *Chemical Engineers Hand-book*, edited by Perry, J. H., 468, eq. 25.
23. *ibid*, 540, eq.'s. 56, 57, 58.
24. NUKIYAMA, S. and TANASAWA, Y., 1940, *Trans. Soc. Mech. Engrs.* (Japan), 6, (22), S7-S8.
25. *Ind. Chem. Eng.*, 1951, 43, 1318.
26. NUKIYAMA, S. and TANASAWA, Y., 1939, *Trans. Soc. Engrs*, (Japan), 4 138.

ON VOLUME - VISCOSITY[1]

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0. A liquid is a material which does not offer resistance to a stress-deviator (commonly spoken of as "stress-differences") when at rest. A stress-deviator of whatever small magnitude will produce a continuous irrecoverable deformation or flow. This causes a reactive resistance in the measure of the rate of the deformation named viscosity and more specifically shear viscosity (η). In the present paper I am not concerned with this phenomenon, but with the reaction of the liquid to the isotropic component of the stress. Under such stress all materials, whether liquids or solids, behave in the same manner. In other words, under isotropic stress liquids have the properties of solids; they are elastic (irrespective of whether they possess elasticity of shape ot not) and in general have also those other rheological properties which are manifest in solids, namely retardation of elastic response, relaxation of elastic stresses, brittle breaking strength and plasticity. It is the purpose of the present paper to express this behaviour in mathematical terms.

1. Let p_{ij} be the stress-tensor, then in every liquid a partial stress

$$p_{ij}^{*} = -p\delta_{ij} \tag{1.1}$$

where p, the "hydrostatic pressure"[2]

$$p = -p_{aa}^{*}/3 \tag{1.2},[3]$$

will be connected with a volume-strain e_v by

$$e_v = -p/k \tag{1.3}$$

where k is the elastic bulk-modulus, which, in general, will be a function of the invariants of the strain-tensor e_{ij} and of temperature. Note that we denote by strain the recoverable part of the deformation.

The rate at which the stress does work per unit volume or the stress-power $\dot{w}$ can be expressed as the sum of a volumetric part $\dot{w}_v$ and a part related to the change of shape. The former is, as far as the first partial isotropic stress is concerned,

$$\dot{w}_v^{*} = -p\ \dot{e}_v = k\ \dot{e}_v\ e_v \tag{1.4}$$

where Newton's dot denotes material differentiation in respect of time.

From this it follows that in a closed cycle the stress-work vanishes. Accordingly, if this (partial) stress were the total reactive stress, the motion of cubical dilatation would take place without dissipation of energy.

2. For real materials this result is in contradiction with the second law of thermodynamics. Kelvin[2] accordingly introduced a resistance which he named "solid viscosity", namely one exhibited by a solid when elastically strained. Voigt[3] established its mathematics. In the same manner as there are (at least) two different moduli of elasticity, there must be (at least) two coefficients of solid viscosity; one concerning change of volume, the other change of shape. Considering that a liquid, as said above, behaves under isotropic stress not differently from a solid, a liquid must have solid volume-viscosity. Let us denote volume-viscosity by ζ and indicate "solid" by the index 's', then a second partial isotropic stress should be $p_{ij}^{**} = \zeta_s\ \dot{e}_v\ \delta_{ij}$ (2.1)

(1) Paper presented at the Eighth International Congress on Theoretical and Applied Mechanics, Istanbul, 1952.
(2) Truesdell has proposed the term "thermodynamic static pressure".
(3) We use the summation-convention and Greek letters for dummy indices.

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and the total isotropic resistance

$$p_{ij} = (k\, e_v + \zeta_s\, \dot{e}_v)\, \delta_{ij} \tag{2.2}$$

from which the mean pressure

$$p_m = -p_{aa}/3 = -(k\, e_v + \zeta_s\, \dot{e}_v) \tag{2.3}$$

which is therefore different from p. Stokes[4] identified p with p_m which was therefore equivalent to assuming $\zeta_s = 0$. This has generally been accepted in classical hydrodynamics, compare *e.g.* Lamb[5] p.574, but Tisza[6] maintains from observations on supersonic absorption that ζ_s does not vanish and then is much larger than the coefficient of shear-viscosity η.

We now have for the stress-power

$$\dot{w}_v = k\, e_v\, \dot{e}_v + \zeta_s\, (\dot{e}_v)^2 \tag{2.4}$$

and while the first term on the right side represents, as before, a conserved potential "free" energy which is mechanically recoverable, the second is dissipated and irretrievably lost as heat, $(\dot{e}_v)^2$ being always positive.

3. In order to determine p_m, one will make use of the stress-equations

$$\partial p_{aj}/\partial x_a + \varrho\,(B_j - x_j) = 0 \tag{3.1}$$

together with the boundary-conditions

$$p_{nj} = p_{aj} \cos(n, x_a) \tag{3.2}$$

Assuming p_m to be known, (2.3) yields on integration

$$e_v = e^{-kt/\zeta_s}\,(e_{v,o} - p_m/\zeta_s \cdot e^{kt/\zeta_s}\, dt) \tag{3.3}$$

where $e_{v,o}$ is the volume strain at the time $t = 0$.

If we apply a constant mean pressure p_m on an unstrained material ($e_{v,o} = 0$), a volume-strain

$$-e_v = p_m/k.(1 - e^{-kt/\zeta_s}) \tag{3.4}$$

is produced. Comparing (3.4) with (1.3), we see that the ultimate strain ($t = \infty$) is the same as in the absence of volume-viscosity, On this account Kelvin pointed out that solid viscosity does not imply less perfect elasticity. There is, however, a lagging or delay of the elastic response, the retardation-time being

$$\tau_{ret} = \zeta_s/k \tag{3.5}$$

When, after attaining at the time $t = T$ some strain $\bar{e}_v$, the pressure is released, the strain will disappear in accordance with

$$e_v = \bar{e}_v\, e^{-t/\tau_{ret}} \tag{3.6}$$

where t is now reckoned from $T = 0$.

The "Newtonian" viscous liquid therefore possesses a "natural" time.

4. While the above considerations apply to any material, whether liquid or solid, the specific property of a liquid, when it is not "ideal", is a viscous resistance in the measure of the tensor

$$f_{ij} = \tfrac{1}{2}(\partial v_i/\partial x_j + \partial v_j/\partial x_i) \tag{4.1}$$

where v is the velocity with which an *irrecoverable* displacement takes place. Therefore, f_{ij} is materially different from $\dot{e}_{ij}$, the latter referring to the velocity of a recoverable displacement. What is re-

coverable can only be known from what is recovered. A complete experiment must therefore include observations after removal of the load, ($t > T$), of the kind expressed by (3.6). While e_v then gradually disappears, $\int_o^T f_v\,dt = \int_o^T f_{aa}\,dt$ will stay put.

Non-vanishing of f_v implies the existence of volume-flow, i.e. a continuous cubical dilatation or change of density progressing in time under constant isotropic stress. Positive volume flow was found by Lee, Reiner and Rigden[7] in asphalt and observed quantitatively by Reiner, Ridgen and Thrower[8], negative volume-flow by Glanville and Thomas[9] in concrete (compare also Reiner[9]). Bosworth has observed volume-flow in solidified carbon-dioxide under isotropic pressure, in tension and in torsion. It should be kept in mind that, rheologically, these materials must be considered as liquids (even if possessing elasticity of shape), the order of magnitude of their coefficient of shear-viscosity being respectively-10^{12}, 10^{17} and 10^{10} poises. Conservation of mass requires, of course, that positive volume-flow is connected with an increase, negative volume-flow with a decrease of voids in the material. However, in accordance with Eyring[12] "a liquid is a binary mixture of molecules and holes", and the materials cited are particular only by the size of their holes which makes volume-flow so pronounced. When the load on the body is kept constant, both positive and negative volume-flow must at some time come to an end, the first through rupture or an ultimate rarefication of the material, the second through its ultimate compaction — but this does not invalidate their character as flow and the process may take geological times.

We now define a coefficient of liquid volume-viscosity ζ_l by

$$f_v = -p_m / \zeta_l \tag{4.2}$$

This equation is analogous with (1.3). Therefore, in analogy with the well known relation between the moduli of elasticity E, G and k,

$$E = 9\,k\,G / (3\,k + G) \tag{4.3}$$

there will be a relation between λ_T, Trouton's coefficient of viscous traction, ζ_l and η, namely

$$\lambda_T = 9\,\zeta_l\,\eta / (3\,\zeta_l + \eta) \tag{4.4}$$

5. We must therefore distinguish between two kinds of volume-viscosity, one (ζ_s) connected with volume-strain, the other (ζ_l) with volume-flow. They have sometimes been confounded(1).

When a material is elastically "incompressible", $k = \infty$ which makes $e_v = 0$. In this case from (1.3) p, being the product of 0 and ∞, is indeterminate. It can, however, still be determined from (3.1) and (3,2) and is therefore not arbitrary. Analogously, for volume-flow to be absent in every case, ζ_l must be $= \infty$ from which $f_v = 0$. For solid viscosity to be absent in every case, ζ_l must be $= 0$. However, for volume-flow and solid viscosity to be absent, these are not necessary conditions. For instance, in laminar deformation or flow the volume of the material does not change, whatever the magnitude of either k or ζ_l. Therefore, as Stokes put it, "In most cases in which it would be interesting to apply the theory of friction of fluids the density of the fluid is either constant or may without sensible error be regarded as constant, or else changes slowly with the time. In the first two cases the results would be the same and in the third nearly the same whether ζ_s were equal to zero or not. Consequently, ... in such cases ... the experiments must not be regarded as confirming ... the theory which relates to supposing ζ_s to be equal to zero" (or ζ_l equal to ∞ as we may add).

Considering that in negative volume-flow the "matter" of the material (Eyring's molecules) flows into the holes, it should be possible to express ζ_l in terms or η(2), resulting in a uni-constant theory of liquid viscosity, similar to the attempted relationship of Cauchy-Poisson in the case of elasticity.

6. When there is both volume-strain and volume-flow, the total rate of cubical dilatation in a loaded body is the sum of two, one recoverable and the other irrecoverable. In the unloaded body there may be a recovering volume-strain, but there will be no volume-flow. We have from (3.3)

$$-\dot{e}_v = \dot{p}_m/\zeta_s - (k/\zeta_s)\,e^{-(kt/\zeta_s)}\,(e_{v\,o} + \int (p_m/\zeta_s)\,e^{kt/\zeta_s}\,dt) \tag{6.1}$$

(1) Also by the present author before the position became clear to him. (Reiner 14,11).
(2) Cf. Reiner[10], p. 485.

Let $\dot{d}_{ij}$ be the tensor of the instantaneous rate of deformation (whether recoverable or not), then

$$-\dot{d}_v = -(\dot{e}_v + \dot{f}_v) = p_m\{(\zeta_s + \zeta_l)/\zeta_s\,\zeta_l\} - (k/\zeta_s)\,e^{-kt/\zeta_s}\,(e_{v,o} + \int (p_m/\zeta_s)\,e^{kt/\zeta_s}\,dt) \qquad (6.2)$$

Differentiating in respect of time, and eliminating the second expression within brackets on the right side of (6.2) yields

$$\dot{p}_m + \ddot{p}_m\{(\zeta_s + \zeta_l)/k\} = -\zeta_l\{\ddot{d}_v + (\zeta_s/k)\,\dddot{d}_v\} \qquad (6.3)$$

which is the volumetric rheological equation of the general viscous liquid.

In order to understand its behaviour, let k, ζ_s and ζ_l be constants so that explicit integration can be carried out. We now perform a number of experiments in imagination:

(i) Let the body be compressed to such extent that its (negative) cubical dilatation is $-d_{v,o}$, and then be released at the time $t = 0$ so that $p_m = \dot{p}_m = 0$. (6.3) is then reduced to a linear differential equation in d, which twice integrated yields

$$d_v - d_{v,\infty} = (d_{v,o} - d_{v,\infty})\,e^{-(kt/\zeta_s)} \qquad (6.4)$$

The part $d_{v,o} - d_{v,\infty}$ of the dilatation is therefore asymptotically ($t = \infty$) recoverable and is the elastic strain. The recovery is delayed, the retardation time being the same (3.5) as in the absence of volume-flow. There is a permanent dilatation $d_{v,\infty}$ which is not recovered.

(ii) Let the dilatation—$d_{v,o}$ be kept constant by gradually reducing p_m as required. Now $\dot{d}_v = \ddot{d}_v = 0$ and (6.3) is a linear differential equation in p_m which on integration yields

$$p_m = p_{m,o}\,e^{-\{kt/(\zeta_s + \zeta_l)\}} \qquad (6.5)$$

The stress $p_{m,o}$ applied to produce $d_{v,o}$ therefore relaxes with a relaxation-time

$$\tau_{rel} = (\zeta_s + \zeta_l)/k \qquad (6.6)$$

Another form for (6.3) is accordingly

$$p_m + \dot{p}_m\,\tau_{rel} = -\zeta_l\,(\dot{d}_v + \ddot{d}_v\,\tau_{rel}) \qquad (6.7)$$

In the Stokesian liquid* $\zeta_s = 0$ and $\zeta_l = \infty$ and then $\tau_{rel} = 0$ and $\tau_{rel} = \infty$

It thus appears that a mechanical model such as proposed by Burgers[15] consisting of an elastic spring and a viscous dashpot coupled in parallel, both with another dashpot in series, offers a suitable representation of the volumetric behaviour of the viscous liquid.

7. There is still $\dot{e}_v$ to be defined. One should not rashly identify it with $\dot{e}_{aa}$. In order to subsume it together with f_v in one and the same quantity $\dot{d}_v$ as in (6.2), the measure must be the same for all three. Now from the definition (4.1) of f_{ij} there results that

$$f_v = \dot{V}/V \qquad (7.1)$$

where V is a volume element made up of a certain quantity of matter and dV the increase of the dilated volume, made up of the same material particles. But $\dot{e}_{aa} = (dV/dt)/V$ only in two cases, namely

(i) when the strain is infinitesimal, so that $de_{aa} = dV/V$, or

(ii) when the strain is measured in accordance with Hencky[16] when

$$e_{aa} = ln\ (V/V_o) \qquad (7.2)$$

where V_o is the unstrained volume.

* Truesdell1 has thus named a very general liquid, with very little historical justification. I propose the term "Truesdell-liquid" in its stead, reserving the term Stokesian liquid for one complying with the above conditions.

In all other cases the measure of $\dot{e}_{aa}$ will be different from the measure of f_v as defined by (7.1) and $\dot{e}_v$ must be determined accordingly. For instance, the compressibility may be given by an empirical equation in which $(V-V_o)/V_o$ is expressed as a function of p, as by Bridgman[17]. Or it may be given theoretically through the definition of a certain measure of strain, such as the Almansi-Hamel measure* in which case

$$V/V_o = (1 - 2\ e_{aa}/3)^{-3/2} \tag{7.3}*$$

and therefore

$$\dot{e}_v = \dot{V}/V_o = \dot{e}_{aa} / [1-(2e_{aa}/3)] \tag{7.4}$$

NOTATION

B	— body force	t	— time
d_{ij}	— tensor of deformation	V	— volume
E	— Young's modulus	V_o	— original volume
e	— basis of natural logarithms	δ_{ij}	— Kronecker's unit-tensor
e_{ij}	— strain tensor	$\dot{W}$	— stress power
e_v	— volume strain	$\dot{W}_v$	— volumetric stress power
$\dot{e}_v$	— rate of volume strain	ζ_l	— liquid volume viscosity
r_{ij}	— flow tensor	ζ_s	— solid volume viscosity
r_v	— volume flow	k	— bulk modulus
G	— shear modulus	λT	— Trouton's coefficient of viscous traction
p	— hydrostatic pressure	τ_{ret}	— retardation time
p_{ij}	— tensor of stress	τ_{rel}	— relaxation time
p_{nj}	— surface traction	ϱ	— density
p_m	— mean pressure		

REFERENCES

1. Truesdell, C., 1950, *J. de Mathematiques* (9), **29**, 215.
2. Kelvin, Lord (Sir W. Thomson), 1865, *Proc. Roy. Soc.*, **14**, 289.
3. Voigt, W., 1890, *Abh. Koenigl. Ges. Wiss.*, Goettingen, **36**, 3.
4. Stokes, G. G., 1845, *Camb. Trans.*, **8**, 287; also 1880, **1**, 75, Cambridge.
5. Lamb, H., 1932, *Hydrodynamics*, Sixth Edition, Cambridge; also 1945, Dover Publications.
6. Tisza, L., 1942, *Phys. Rev.*, **61**, 531.
7. Lee, A. R., Reiner, M. and Rigden, P., 1946, *Nature*, **158**, 706.
8. Reiner, M., Rigden, P. and Thrower, E. N., 1950, *J. Soc. Chem. Ind.*, **69**, 257.
9. Glanville, W. H. and Thomas, F. C., 1939, *Building Research Technical Papers*, 21.
10. Reiner, M., 1949, *Appl. Scient. Res.*, **A1**, 475.
11. Bosworth, R. C. L., 1949, *Austral. J. Res.*, (A)2, 394.
12. Eyring, J., 1936, *Chem. Phys.*, **4**, 283.
13. Reiner, M., 1946, *Am. J. Math.*, **68**, 672.
14. Reiner, M., 1951, *Qu. Appl. Math.*, **8**, 341.
15. Burgers, J. M., 1935, *First Report on Viscosity and Plasticity*, Amsterdam.
16. Hencky, H. Z., 1928, *Techn. Phys.*, **9**, 214, 457.
17. Bridgman, P. W., 1949, *Am. Acad. Arts Sciences*, **77**, 129,
18. Truesdell, C., 1952. *Journal rat. Mech. and Analysis*, **1**. 125.

* Compare Truesdell 18, § 15.

THE PHOTOCHEMICAL DEHYDROGENATION OF BIANTHRONE DERIVATIVES

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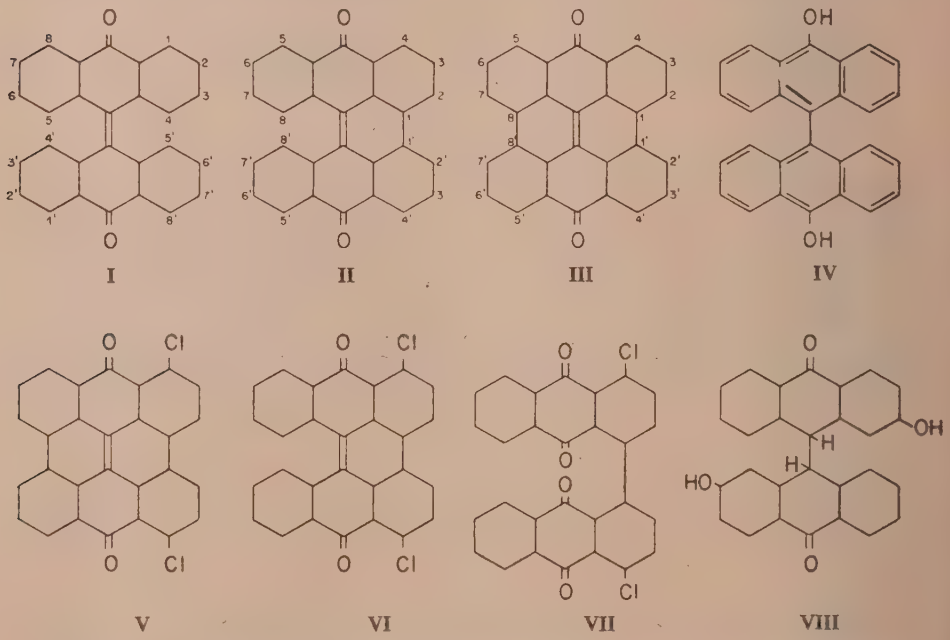
The phenomena of thermochromy[1-10] and photochromy[11-13] exhibited by bianthrone (I) and the influence of substituents on them, such as the inhibition of the thermochromy by substituents in the 4,4'-positions[14-16], have led us to a renewed study of the well-known photochemical dehydrogenation of bianthrones to helianthrones (II) and naphthodianthrones (III), in which the hydrogen atoms of the positions next to the central bond are involved. Particular interest is attached to this reaction in view of the discovery[17,18] that the photodynamically active natural compounds of the fagopyrin and hypericin type belong to the series of bianthrone and naphthodianthrone.

A solution of bianthrone (I) deposits, upon exposure to sunlight, the highly insoluble naphthodianthrone (III)[1b]; the same compound is obtained from helianthrone (II) under the influence of light or aluminium chloride[19]. If the photochemical dehydrogenation of (I) was interrupted prematurely, bianthranol (IV) could be isolated; if acetic anhydride was used as solvent, the diacetate of (IV) could be obtained instead[1b] upon such interruption.



The influence of substituents on these reactions has been elucidated to some extent[1d], although the results have been obscured by errors in the assignment of formulae to intermediate products (see, e.g., Barnett and Matthews[20]). Thus, 1,1'-dichloro-bianthrone was found to be converted photochemically into a dichloro-naphthodianthrone (V); this could also be obtained by dehydrogenation (photochemically, with aluminium chloride or chromic acid) of the dichloro-helianthrone (VI) which is formed from 1,1'-dichloro-4,4'-bis-anthraquinonyl (VII) with copper in concentrated sulphuric acid.

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The following bianthrone derivatives are converted stepwise into the corresponding helianthrones and naphthodianthrones:

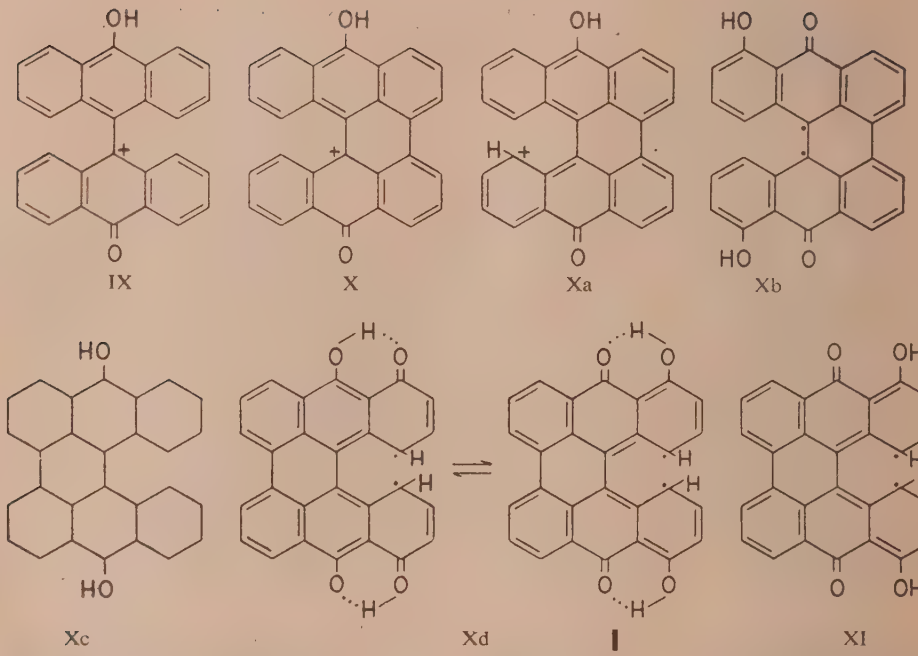
3,3'-dichloro[1d]
3,3'-dimethyl[21]
1,1'-dimethoxy[21,22]
3,3'-dimethoxy[21]
2,3,2',3'-tetramethoxy-[21]
1,1',6,6',8,8'-hexahydroxy
3,3'-dimethyl ("Oxypenicilliopsin")[17]
1,8,1',8'-tetrachloro.[1d]

In the helianthrone series, the following cases of photochemical conversion into naphthodianthrones have been recorded:

2,2'-diacetoxy-helianthrone in benzene[23]
2,2'-dimethyl-helianthrone in acetic acid[24]
4,4'-dimethoxy-helianthrone in chlorobenzene[22]
3,3',4,4'-tetrahydroxy-helianthrone in nitrobenzene, not in pyridine[22,25,26]
4,4'-dihydroxy-helianthrone in conc. sulphuric acid[25]
4,4',5,5'-tetramethoxy-helianthrone in conc. sulphuric acid[25,27]
3,3'-dimethyl-4,4'-dimethoxy-helianthrone in conc. sulphuric acid[28]
2,2'-dimethyl-4,4'-dimethoxy-helianthrone in conc. sulphuric acid[28]
2,2'-dimethyl-4,4'-dihydroxy-helianthrone in conc. sulphuric acid[28]
2,2'-dimethyl-4,4'-diacetoxy-helianthrone in conc. sulphuric acid, but also in organic solvents[28]
2,2,'-dimethyl-4,4',5,5',7,7'-hexahydroxy-helianthrone pentamethylether in acetone[28a]

This compilation shows that the ease with which the photochemical dehydrogenation takes place is dependent on the nature and the position of the substituents; however, no quantitative kinetic data are available. It may be useful to recall some other, equally qualitative observations, on the differential reactivities of some substituted bianthronyls and helianthrones. The hydroxyl groups in 3,3'-dihydroxy-bianthronyl (VIII) and the corresponding 2,2'-diiodo-compound activate the 4,4'-(and 5,5') positions so much that the substances are converted by potassium ferricyanide directly into 2,2'-dihydroxy-helianthrone and its iodo-derivative, respectively[29,30]. Iodine in pyridine converts 1,1'-dihydroxy-2,2'-dimethoxy-bianthronyl into 4,4'-dihydroxy-3,3'-dimethoxy-helianthrone (and 2,6-dihydroxy-3,7-dimethoxy-*hetero*-coerdianthrone).[30a] Thirdly, the treatment of 3,3'.4,4'-tetrahydroxy-helianthrone with acetic anhydride and pyridine gives not only the corresponding tetraacetoxy-compound, but 3,3'4,4'-tetracetoxy-naphthodianthrone[26]. It appears, therefore, that 2-(or 6-) hydroxy-groups in bianthronyl and bianthrone and 3-hydroxy-groups in helianthrone enhance the dehydrogenability, whilst 4-hydroxy-groups in helianthrone impede it; this inhibition, however, is overcome in concentrated sulphuric acid. In this solution, the dehydrogenation, sometimes, takes place already without the influence of light, e.g. by raising the temperature of the solution[25].

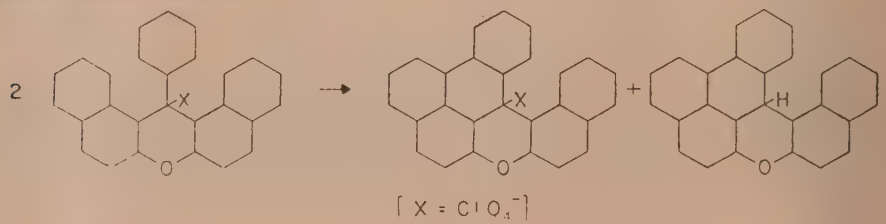
Recent spectrographic investigation of the solutions of bianthrone, helianthrone and naphthodianthrone in conc. sulfuric acid[31] has led to the conclusion that these compounds form halochromic salts of the type (IX, X); these, then, are the molecular species on which the photo-dehydrogenation occurs in such solutions — the same assumption has also been made by Brockmann *et al.*[25] — and one is led to conclude that (X) undergoes dehydrogenation in the resonance structure (Xa). In the normal, organic solvents, an ionic mechanism is unlikely, and one will have to postulate an analogous "*free radical*" mechanism, the simplest assumption being that the π-electrons of the central double bond are uncoupled (X b). Formation of the resonance structure Xc will then initiate the dehydrogenation. In this case, the inhibiting effect of hydroxyl groups in the immediate vicinity of the carbonyl group would be due to the formation of a strong hydrogen bond between them (X d), as it has been suggested in the explanation of the course of the reduction of 1-hydroxy-anthraquinone.[21,cf.37] Methoxyl groups, therefore, in the 4-position of helianthrone do not exert the same inhibiting influence as hydroxyl groups. It should be noted that Xd contains a normal naphthalene system which may well contribute to its stabilisation.



Indeed, Brockmann *et al.*[32] have already pointed out that this dehydrogenation is analogous to the usual dimerising oxidation of phenols, for which analogous regularities have been observed by previous authors[33,34,35,35a] and it will be shown that all existing data fit into this picture of the process.

The above speculations are supported by existing data on the *mechanism* of the photochemical dehydrogenation[1b,36]. In the first step of the dehydrogenation of bianthrone and helianthrone, these substances act themselves as hydrogen acceptors, giving bianthranol (as IV) and helianthranol (XI), respectively. (In this stage, too, the 4,4'-hydroxyl groups of helianthrone (1,1' in bianthrone) may prevent the carbonyl groups from taking up the hydrogen). In acetic anhydride, the corresponding diacetates are formed. The bianthranol and helianthranol are then dehydrogenated by oxygen (formation of hydrogen peroxide) or in the absence of oxygen by other, added oxidation agents, and the reaction continues. If neither of these — secondary — hydrogen acceptors is present, the reaction of bianthrone leads to one mole of naphthodianthrone and two moles of bianthranol, that of helianthrone to equimolar quantities of naphthodianthrone and helianthranol.

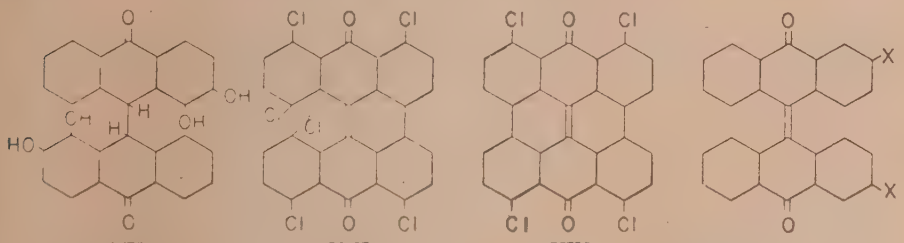
The kinetic investigation of the photochemical dehydrogenation of helianthrone showed that the reaction is independent of the concentration. The reaction can, therefore, not be strictly bimolecular, but must be composed of a slow reaction, *e.g.* the activation of the helianthrone molecule — as indicated above – and a fast step, which would be the transfer of the hydrogen from the activated to a normal helianthrone molecule. It is interesting that the cyclising disproportionation of phenyldibenzoxanthenium perchlorate[38]

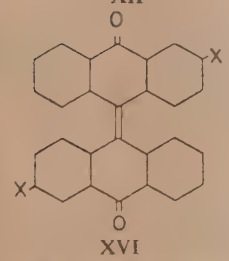


which is also a photochemical reaction, was found to be equally independent of the concentration of the compound and that the quantum yield is approximately equal in both cases (3—5% per C-C bond formed). Analogous considerations can be applied to the dehydrogenation of bianthrone to naphthodianthrone.

It is also in accord with this theory that antioxidants (phenols, piperidine, pyridine, hydroquinone, aniline) inhibit the photochemical dehydrogenation.

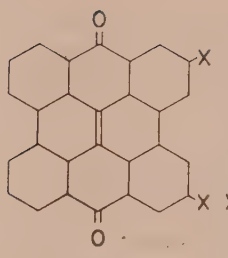
Of particular interest in this connection is the behaviour of those bianthrones or helianthrones which contain substituents in the positions required for the cyclisation. 3,4,3′,4′-Tetrahydroxy-bianthronyl (XII) and the corresponding tetramethoxy compound cannot be dehydrogenated by any means[21,39] and 4,5,8,4′,5′,8′,-hexachloro-helianthrone (XIII)remains unchanged upon irradiation in nitrobenzene or xylene as solvent: in conc. sulfuric acid, however, hydrogen chloride and some chlorine is liberated, yielding (XIV)[40]. Analogous observations have been made in the case of 1,4,1′,4′-tetrachlorobianthrone[1d]. This is explicable by the mechanism outlined above; it recalls the easy elimination of the halogen atoms from the benzene nuclei of *p*-halogenated triphenylmethyl salts.



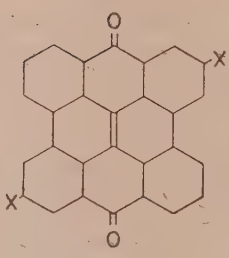


A last point has to be considered. The photochemical dehydrogenation of a bianthrone of the general formula (XV) can give two different naphthodianthrones (XVII, XVIII) via the corresponding helianthrones (XIX, XX), as the geometrical structure of (I) is not generally known and no isomeric pairs such as (XV, XVI) appear to exist. Only in one known case[30] a definite statement can be made: 1-Bromo-2-benzyloxy-anthraquinone (XXI) can be converted into the same bianthraquinonyl derivative (XXII) which is obtained by careful oxidation of 2,2'-dihydroxy-helianthrone (XIX or XX, X = OH). Hardacre and Perkin[30] conclude rightly that the helianthrone is the *cis*-compound (XIX). Similar, but more tentative considerations have been put forward by Brockmann *et al.*[32], in order to explain the fact that hypericin has a *cis*-structure.

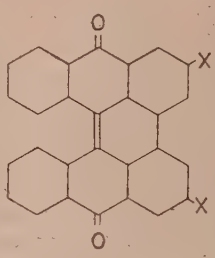
In the present investigation which is concerned with simply substituted bianthrones, some more data as to the configuration of these bianthrones have come to light. Schmidt[41] has shown by X-ray analysis of the solid substances, that the bianthrones derived from 4-methyl- and 4-bromo-anthrone appear to have *trans*-configurations, i.e. the structure of 4,5'-dimethyl- and 4,5'-dibromo-bianthrone, respectively. A number of 2,2'-disubstituted bianthrones, which have been prepared[15], did not crystallise well enough to permit an X-ray investigation; it should, however, be pointed out that the chromatography on active alumina using chloroform both as solvent and eluent, failed to give any separation into different fractions on these compounds. (In general, the bianthrones can very efficiently be purified by this method). Also dipole moment measurements on 2,2'-(2,3')-dibromobianthrone, which should have differentiated between the *cis*-structure ($\mu = 2.95$) and the *trans*-form ($\mu = 0$), proved impossible because of the insufficient solubility of the compound in non-polar solvents.



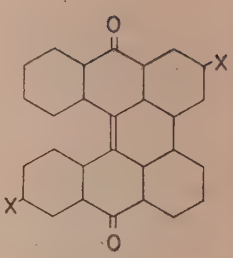
XVII



XVIII



XIX



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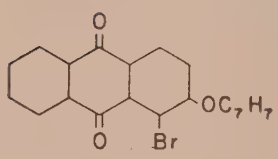
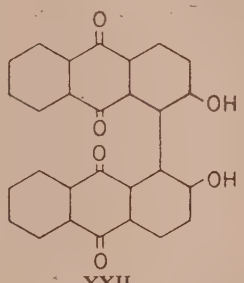
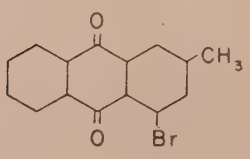


XXI

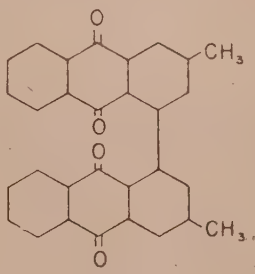


XXII

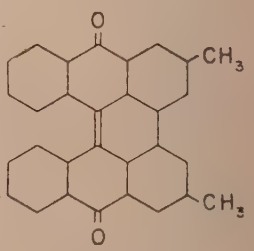
Recourse was, therefore, taken to chemical methods. *If one assumes that the photochemical dehydrogenation does not involve any change in the configuration of the starting material*, a 2,2'-disubstituted bianthrone (XVI) should give a 3,6'-disubstituted naphthodianthrone (XVIII), the 2,7'-disubstituted isomer (XV) a 3,3'-disubstituted naphthodianthrone (XVII). In the case of the 2,2'-(or 2,7'-) dimethyl-compound, 3,3'-dimethylnaphthodianthrone (XVII, $X = CH_3$) was synthetised according to **Ruggli**[42], from 1-bromo-3-methyl-anthraquinone (XXIII) as follows:



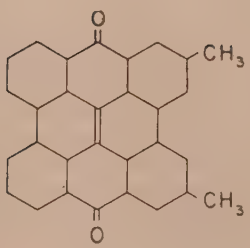
XXIII



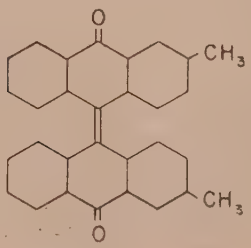
XXIV



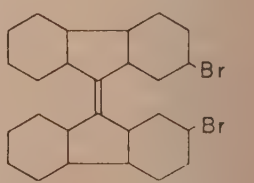
XXV



XXVI



XXVII



XXVIII

Treatment with copper at high temperature gave the bianthraquinonyl derivative (XXIV), which could be reduced to the helianthrone (XXV); this, upon irradiation, gave the naphthodianthrone (XXVI). As the melting point of this compound as well as that of the photo-dehydrogenation product from the dimethylbianthrone lies above 500°, the method of mixed melting points appeared inadequate for the identification of the two compounds. (Sauvage[43] determined the m.p. of the unsubstituted naphthodianthrone as 600—602°). However, the X-ray powder diagrams of the two products established their identity. With the above formulated reservation, therefore, the dimethylbianthrone has *cis*-configuraration (XXVII). In this respect, it should be recalled that in the case of 2,2'-dibromo-dibiphenyleneethene (XXVIII), too, the one known compound has the *cis*-structure[44].

When, however, 3,3'-dibromo-naphthodianthrone was synthetised from 1,3-dibromo-anthraquinone[45], it was shown to be different from the photo-dehydrogenation product of 2,2'-(2,7')-dibromobianthrone. It appears, therefore, that the latter is the *trans*-form (2,7'-dibromo-compound), if a conclusion may be derived from a negative result.

PHOTO-OXIDATION EXPERIMENTS

All the 2,2'-(2,7')- and 3,3' (3,6')-disubstituted bianthrones which have been studied gave naphthodianthrones on irradiation in solution. It seemed therefore of interest to investigate whether the general mechanism, established for the photooxidation of bianthrone, was valid also for its substitution products, and how far the course of the reaction was influenced by the position and nature of the substituents.

The general procedure was irradiation of a weighed amount of the bianthrone in boiling acetic anhydride in the presence of fused sodium acetate, followed by filtering and weighing of the naphthodianthrone formed, and by examination of the filtrate for the presence of the corresponding disubstituted bianthranol diacetate. Direct sunlight was used for all irradiations. It is recalled that theoretically one third of the bianthrone should be converted into the corresponding naphthodianthrone.

In Brockmann's experiments[36], the amount of naphthodianthrone formed was more than one third, a fact which was explained by him by assuming that some of the bianthranol formed was oxidised by air before it had a chance to be acetylated by the solvent.

The results obtained with 2,2'-dibromo- and 2,2'-dimethyl-bianthrone strikingly justified Brockmann's mechanism. In the former, there was observed a conversion of 34%, in the latter one of 39%, to the corresponding naphthodianthrone. From the filtrate, after purification, substances were obtained, which were identified as the corresponding bianthranol diacetates, by the determination of their mixed melting points with authentic specimens.

With 3,3'-dibromo-bianthrone the reaction was more sluggish; after six hours of irradiation only a 19% conversion to the naphthodianthrone occurred. But in this case, too, 3,3'-dibromo-bianthranol diacetate was obtained from the filtrate.

The photooxidation of these 2,2'- and 3,3'-disubstituted bianthrones proceeded smoothly also in other solvents, such as xylene, chloroform or nitrobenzene, but not in aniline.

4,5'-Dimethylbianthrone, which was studied as an example of the 4,5'-disubstituted bianthrones, remained completely unchanged under these condtions as well as in other solvents.

4,5'-*Dibromo*-bianthrone, on the other hand, gave an unexpected result, when its solutions in pyridine or xylene were exposed to sunlight. An insoluble compound was quickly formed, which was identified as naphthodianthrone (III), by comparison of its X-ray powder photograph with that of an authentic specimen. At the same time, hydrogen bromide was liberated. Titration (by the potentiometric method of Cavanagh[46]) showed that approximately two molecules of hydrogen bromide were formed for each molecule of naphthodianthrone. The reaction proceeded to completion in the absence of air, and is the more surprising as the C-Br bond in 4,5'-dibromo-bianthrone has the normal strength: the compound was, e.g., recovered unchanged when its solution in xylene was refluxed, in darkness, with mercury or sodium amalgam.

Irradiation of the compound in boiling acetic anhydride showed that in this case, too, the photoreaction produced the corresponding bianthranol. Its diacetate was formed, however, in much smaller amounts than usual, while the conversion to naphthodianthrone was accomplished to an extent of 60—90%. In this case, the hydrogen bromide formed amounted to less than two molecules for each molecule of naphthodianthrone.

This photochemical dehydrohalogenation reaction also has its counterpart in the photochemical elimination of hydrogen chloride from (*o*-chlorophenyl)-dibenzoxanthenium perchlorate[47].

As experiments in pyridine showed that the reaction rate is dependent on the concentration, the process cannot be accomplished in one step, and the experiments will have to be explained, at least qualitatively, by the assumption that in the first instance the two "ortho" hydrogen atoms are eliminated and absorbed by a second molecule of dibromo-bianthrone, giving the dibromo-bianthranol. Then the two bromine atoms are removed and oxidise the latter again to dibromo-bianthrone. If the dibromo-bianthranol is stabilised by acetylation, the bromine atoms must react otherwise, e.g., giving a bromine molecule (which has not been identified). In addition, direct conversion of dibromo-bianthrone into naphthodianthrone and 2 moles of hydrogen bromide may take place.

EXPERIMENTAL

The *bianthranol diacetates* were prepared by refluxing the dry bianthranol (0.3 g) with acetic anhydride (3 cc), in the presence of some fused sodium acetate, for twenty minutes. The reaction mixture was cautiously decomposed with water, and the solid which separated purified by passing its chloroform solution through a column of activated alumina, followed by concentration of the eluate and precipitation with methanol and recrystallisation of the product. All compounds exhibited blue to violet fluorescence in benzene solution.

4,4'-*Dibromo-bianthranol diacetate*. Crystallisation from a benzene-heptane mixture gave yellow, diamond-shaped prisms of m.p. 260—261°. *Anal.* Calcd. for $C_{32}H_{20}O_4Br_2$; acetyl, 13.7. Found: acetyl, 14.0.

3,3'-*Dibromo-bianthranol diacetate*. Very small, short, yellow prisms of m.p. 339—340°. *Anal.* Calcd. for $C_{32}H_{20}O_4Br_2$: Br, 25.4. Found: Br, 25.8.

2,2'-*Dimethyl-bianthranol diacetate*. Small yellowish needles, from a mixture of benzene and heptane; m.p. 267—268°. *Anal.* Calcd. for $C_{34}H_{26}O_4$: C, 81.9; H, 5.3. Found: C, 81.7; H, 5.4.

2,2'-*Dibromo-bianthranol diacetate*. Light yellow crystals, from a mixture of chloroform and methanol; m.p. 301—302°. *Anal.* Calcd. for $C_{32}H_{24}O_4Br_2$: acetyl, 13.7. Found: acetyl, 14.0.

Synthesis of 3,3'-*dimethyl-naphthodianthrone* (XVII, $X = CH_3$)[42]. 2-Methyl-anthraquinone was nitrated to 2-methyl-1-nitro-anthraquinone, according to Locher and Fierz[48]. Reduction with sodium sulphide gave 2-methyl-1-amino-anthraquinone. This was brominated to the 4-bromo-compound and the latter deaminated to 3-methyl-1-bromo-anthraquinone (XXIII), which was then converted to 3,3'-dimethyl-bianthraquinonyl (XXIV) with copper in nitrobenzene. M.p. 361—363° (literature[42]: 354—355°) By reduction with copper powder in concentrated sulphuric acid in the usual manner, 3,3'-dimethyl-helianthrone (XXV) was obtained. This was purified by chromatography on active alumina from chloroform, followed by crystallisation from the same solvent to give orange yellow needles, m.p. 357—358° (literature[42]; above 300°).

Irradiation of 3,3'-dimethyl-helianthrone (XXV) in pyridine solution gave the naphthodianthrone (XXVI) in practically quantitative yield. This compound has been prepared previously by the same route[49].

Dimethyl-naphthodianthrone from 2,2'-*dimethyl-bianthrone*. 2,2'-Dimethyl-bianthrone (97 mg) wa dissolved in pyridine (15 cc) at room temperature, and the solution exposed to sunlight for two hours. The yellow dimethyl-naphthodianthrone (48 mg) was filtered off, washed with pyridine and dried. More was obtained by further exposing the filtrate to light.

The X-ray powder photograph of this compound was identical with that of the synthetic product.

Synthesis of 3,3'-*dibromo-naphthodianthrone*[45]. 2-Amino-anthraquinone was brominated to the 1,3-dibromo-compound, and the latter deaminated to 1,3-dibromo-anthraquinone, which was converted into 3,3'-dibromo-bianthraquinonyl in the usual way. M.p. 380° (literature:[45] 397°). Reduction with

copper in sulphuric acid gave 3,3'-dibromo-helianthrone[1d], yellow needles from bromobenzene, m.p. 380°. Irradiation of this compound in pyridine solution gave 3,3'-dibromo-naphthodianthrone in practically quantitative yield.

Anal. Calcd. for $C_{28}H_{10}O_2Br_2$: Br, 29.7. Found: Br, 30.7.

Dibromo-naphthodianthrone from 2,2'-(2,7') -dibromo-bianthrone. This bianthrone (130.6 mg) was dissolved in pyridine (20 cc) and the solution irradiated for four hours. The naphthodianthrone obtained weighed 50.6 mg; more was obtained on exposure of the filtrate to sunlight.

Anal. Calcd. for $C_{28}H_{10}O_2Br_2$: Br, 29.7. Found: Br, 28.7.

The X-ray powder photograph of this compound was not identical with that of the synthetic product.

Photo-oxidation experiments

1) 2,2'-*Dimethyl-bianthrone*

The compound (124 mg; 0.30 mMol) was disolved in redistilled acetic anhydride (40 cc), and fused sodium acetate (0.2 g) was added. The mixture was refluxed in direct sunlight for four hours. The insoluble yellow dimethyl-naphthodianthrone was filtered, washed with acetic acid and water, and dried. The weight was 48 mg (0.118 mMol, 39% conversion).

The filtrate was evaporated to dryness, the residue taken up in benzene and the solution filtered from sodium acetate and chromatographed on active alumina. Elution of the lower, yellowish zone with a benzene-methanol mixture (10:1), followed by concentration of the elutate and crystallisation of the residue from dilute methanol, gave yellowish material of m.p. 261—265°, which did not depress the melting point of an authentic specimen of 2,2'-dimethyl-bianthranol diacetate.

2) 2,2'-*Dibromo-bianthrone*

This compound (212 mg; 0.39 mMol) was dissolved in acetic anhydride (45 cc) in the presence of sodium acetate (0.2 g), and the mixture was refluxed in sunlight for four hours. The dibromo-naphthodianthrone obtained weighed 71.8 mg (0.133 mMol; 34% conversion). Working up the filtrate, as for the previous compound, gave after chromatography a yellowish solid of m.p. 295°. The mixed m.p. with 2,2'-dibromo-bianthranol diacetate was 297—299°.

The above experiment was repeated, using 61 mg (0.112 mMol) of the compound, 15 cc of acetic anhydride, and 0.05 g of sodium acetate. This time the apparatus was filled with pure nitrogen. The dibromo-naphthodianthrone obtained weighed 21.0 mg (0.039 mMol; 35% conversion).

3) 3,3'-*Dibromo-bianthrone*

This compound (160.9 mg; 0.297 mMol) was dissolved in acetic anhydride (52 cc) together with fused sodium acetate (0.2 g). The solution was refluxed in sunlight for six hours. The dibromo-naphthodianthrone obtained weighed 29.8 mg (0.0554 mMol; 19% conversion). The filtrate was worked up as for the previous two compounds. After chromatography from chloroform solution, a yellow crystalline solid was obtained, of m.p. 341°, which was identified as 3,3'-dibromo-bianthranol diacetate.

4) 4,5'-*Dimethyl-bianthrone*

This compound (64.7 mg) was dissolved in a minimum (18 cc) of acetic anhydride at the boiling point in the presence of fused sodium acetate (0.1 g). The solution was refluxed in sunlight for six hours. No change in colour was observed and no precipitation took place. On cooling overnight, the unchanged material which crystallised out was filtered, washed and dried. Thus 61 mg was recovered.

5) 4,5'-*Dibromo-bianthrone*

(a) *Irradiation in pyridine at room temperature.* The compound (70.5 mg; 0.13 mMol) was dissolved in freshly distilled pyridine (20 cc), and the solution was exposed to sunlight for six hours, with occasional shaking. The naphthodianthrone formed was filtered, washed with pyridine (5 cc) and distilled water, and dried to constant weight. Yield, 51.0 mg (0.133 mMol).

To the filtrate, nitric acid (23% w v; 70 cc) was added; the solution was diluted with water and the bromide ion determined, using silver bromide and quinhydrone electrodes[46]. (It was found that an excess of acid led to erratic, and excess of pyridine to uniformly high, results). Thus, 0.252 mMol of HBr were found, so that its ratio to naphthodianthrone was 1.9.

The following experiment was carried out in the same manner, but in an atmosphere of hydrogen. A quantity of 24.9 mg (0.045 mMol) in 15 cc of pyridine gave within four hours of exposure 11.2 mg (0.045 mMol) of naphthodianthrone and 0.095 mMol of HBr. Ratio: 2.13.

The identity of the naphthodianthrone obtained in these two experiments was checked by comparing its X-ray powder photograph with that of the authentic compound, obtained by the irradiation of bianthrone in pyridine.

(b) *Irradiation under acetylating conditions.* A weighed amount of the compound was dissolved in redistilled acetic anhydritde, an approximately equal amount of sodium acetate was added, and the mixture was refluxed in sunlight for four to six hours. The naphthodianthrone formed was filtered off, washed with acetic acid and water, and dried.

The filtrates were evaporated to dryness in vacuo, and the residue treated and purified as described for 2,2'-dimethyl-bianthrone. The compound thus obtained had m.p. 260—261°; the mixed m.p. with 4,5'-dibromo-bianthranol diacetate was 259—261°.

Results

Bianthrone derivative		Acetic anhydride	Naphthodianthrone		Conversion
mg	mMol	cc	mg	mMol	%
62.5	0.115	20	27.4	0.072	62.6
42.5	0.075	15	22.4	0.059	75
31.5	0.058	8	18.0	0.047	81

The following experiments were carried out under pure nitrogen.

Bianthrone derivative		Acetic anhydride	Naphthodianthrone		Conversion
mg	mMol	cc	mg	mMol	%
77.9	0.144	20	37.9	0.098	68
41.6	0.077	15	19.9	0.052	67.5

The rather dark naphthodianthrone obtained in one of these experiments was analysed for bromine; it contained only traces (1.9%).

In the following experiment, a weighed amount of the compound was dissolved in pyridine, acetic anhydride was added, and the mixture was exposed to sunlight for four hours at room temperature. The naphthodianthrone was filtered, washed with pyridine and distilled water, and dried and the filtrated titrate for hydrogen bromide.

Bianthrone derivative		Pyridine	Acetic anhydride	Naphthodianthrone		HBr	Ratio HBr/Naphthodianthrone	Conversion
mg	mMol	cc	cc	mg	mMol			%
44.4	0.082	10	2.8	29.8	0.078	0.139	1.78	95.7
68.0	0.126	12	12.0	38.3	0.10	0.165	1.65	83.5

This investigation forms part of a thesis submitted by Mr. H. J. E. Loewenthal to the University of London in partial fulfilment of the requirements for the degree of Ph. D.

REFERENCES

1. (a) MEYER, H., 1909, *Monatsh.*, **30**, 165.
(b) MEYER, H., BONDI, A. and ECKERT, A., 1912, *Monatsh.*, **33**, 1447.
(c) MEYER, H. and ECKERT, A., 1918, *Monatsh.*, **39**, 241.
(d) ECKERT, A. and TOMASCHEK, R., 1918, *Monatsh.*, **39**, 839.
2. SCHOENBERG, A. and SCHUETZ, O., 1928, *Ber.*, **61**, 468.
3. SCHOENBERG, A., ISMAIL, A.F.A. and ASKER, W., 1946, *J. Chem. Soc.*, 442.
4. BERGMANN, E. and ENGEL, ST., 1930, *Z. physikal. Chem.*, **B8**, 135.
5. BERGMANN, E. and CORTE, H., 1933, *Ber.*, **66**, 39.
6. BERGMANN, E., 1948, *Isomerism and Isomerization*, New York.
7. BERGMANN, E., HIRSHBERG, Y. and LAVIE, D., 1952, *Bull. Soc. Chim. France*, **19**, 268.
8. PULLMAN, B., PULLMAN, A., BERTHIER, G. and PONTIS, J., 1952, *Bull. Soc. Chim. France*, **19**, 271.
9. GRUBB, W. T. and KISTIAKOWSKY, G. B., 1950, *J. Amer. Chem. Soc.*, **72**, 411.
10. THEILACKER, W., KORTUEM, G. and FRIEDHEIM, G., 1950, *Ber.* **83**, 508.
11. HIRSHBERG, Y., LOEWENTHAL, E., BERGMANN, E. and PULLMAN, B., 1951, *Bull. Soc. Chim. France*, **18**, 88.
12. HIRSHBERG, Y., 1950, *Compt. Rend.*, **231**, 903. *Cf.* FISCHER, E. and HIRSHBERG, Y., 1952, *J. Chem. Soc.* 4522
13. HIRSHBERG, Y., 1951, *Bull. Res. Council of Israel*, **1**, No. 3., 123.
14. HIRSHBERG, Y., LOEWENTHAL, E. and BERGMANN, E., 1951, *Bull. Res. Council of Israel*, **1**, No. 1-2, 139.
15. BERGMANN, E. and LOEWENTHAL, E., 1952, *Bull. Soc. Chim. France*, **19**, 66.
16. BERGMANN, E. and LOEWENTHAL, E., 1953, *J. Chem. Soc.*, in press.
17. For a review, see Brockmann, H., in *Progress in Organic Chemistry*, Vol. I, p. 64 (New York and London, 1952).
18. *Cf.* BROCKMANN, H. and co-workers, 1951, *Naturwiss.*, **38**, 141; 1950, *Ber.*, **83**, 583.
19. SCHOLL, R. and MANSFELD, H., 1910, *Ber.*, **43**, 1745.
20. BARNETT, E. de B. and MATTHEWS, M. A., 1923, *J. Chem. Soc.*, **123**, 2549.
21. ATTREE, G. F. and PERKIN, A. G., 1931, *J. Chem. Soc.*, **144**.
22. ECKERT, A., and HAMPEL, J., 1907, *Ber.*, **60**, 1693.
23. HALLER, J. W. E. and PERKIN, A. G., 1924, *J. Chem. Soc.*, **125**, 231.
24. BROCKMANN, H., POHL, F., MAIER, K. and HASCHAD, M. N., 1942, *Ann.*, **533**, 1.
25. BROCKMANN, H., LINDEMANN, E., RITTER, K. H. and DEPKE, F., 1950, *Ber.*, **83**, 583. *Cf.* KORTUEM, G., THEILACKER, W., ZEININGER, H. and EILLIEHAUSEN, H., 1953, *Ber.*, **86**, 294.
26. PERKIN, A. G. and HADDOCK, N. H., 1933, *J. Chem. Soc.*, 1512.
27. BROCKMANN, H., NEEF, R. and MUEHLMANN, R., 1950, *Ber.*, **83**, 467.
28. BROCKMANN, H. and DORLARS, A., 1952, *Ber.*, **85**, 1168.
28a. BROCKMANN, H. and MUXFELDT, H., 1953, *Naturwiss.*, **40**, 411.
29. PERKIN, A. G. and YODA, G., 1925, *J. Chem. Soc.*, **127**, 1884.
30. HARDACRE, R. W. and PERKIN, A. G., 1929, *J. Chem. Soc.*, 180.
30a GOODALL, F. L. and PERKIN, A. G., 1924, *J. Chem. Soc.*, **125**, 470.
31. HEBERT, R. A., GOREN, M. B. and VERNON, A. A., 1952, *J. Amer. Chem. Soc.*, **75**, 5779.
32. BROCKMANN, J., v. FALKENHAUSEN, E. H., NEEFF, R., DORLARS, A. and BUDDE, G., 1951, *Ber.*, **84**, 865.
33. GOLDSCHMIDT, S., SCHULZ, E. and BERNARD, H., 1929, *Ann.*, **478**, 1.
34. PUMMERER, R., PUTTFARKEN, H. and SCHOPFLOCHER, R., 1925, *Ber.*, **58**, 1808.
35. COSGROVE, S. L. and WATERS, W. A., 1951, *J. Chem. Soc.*, 1726.
35a PUMMERER, R., SCHMIDUTZ, G. and SEIFERT, H., 1952, *Ber.*, **85**, 535.
36. BROCKMANN, H. and MUEHLMANN, E., 1949, *Ber.* **82**, 348.
37. WILES, L. A., 1952, *J. Chem. Soc.*, 1358.
38. HERTEL, E. and SOCK, G., 1941, *Z. physikal. Chem.*, **A189**, 95.
39. MACMASTER, A. and PERKIN, A. G., 1927, *J. Chem. Soc.*, 1306.
40. ECKERT, A., 1925, *Ber.*, **58**, 322.
41. SCHMIDT, G. and HARNICK, O., unpublished results.
42. RUGGLI, P. and MERZ, E., 1929, *Helv. Chim. Acta*, **12**, 71.
43. SAUVAGE, G., 1947, *Ann, Chim.*, (12), **2**, 869.
44. BERGMANN, E., BERTHIER, G., FISCHER, E., HIRSHBERG, Y., LOEWENTHAL, E., PULLMAN, B. and LAVIE, D., 1952, *Bull. Soc. Chim. France*, **19**, 78.
45. ULLMANN, F. and EISER, H., 1916, *Ber.*, **49**, 2154.
46. CAVANAGH, B., 1927, *J. Chem. Soc.*, 2207.
47. DILTHEY, W. and QUINT. F., 1936, Ber., **69**, 1515.
48. LOCHER, A. and FIERZ, DAVID., H. E., 1927, *Helv. Chim. Acta*, **10**, 642.
49. BROCKMANN, H. and RANDEBROCK, R., 1951, *Ber.*, **84**, 543.

THORIUM TARTRATE COMPLEXES: THEIR COMPOSITION, STRUCTURE AND BEHAVIOUR

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The experiments discussed in this report are analogous to those carried out in connection with the study of thorium citrate[1]. No special investigation devoted to thorium tartrate has appeared recently[2-5] As in the previous investigation, "Heterometric" measurements were used as a basis for the study of the heterogeneous reactions taking place in solutions containing thorium and tartrate.

EXPERIMENTAL

Reagents and solutions

Stock solutions of thorium nitrate and sodium tartrate were prepared by weighing the salts $Th(NO_3)_4 \cdot 4H_2O$ and $Na_2C_2H_4O_6 \cdot 2H_2O$ (C.P. Baker's Analyzed), and solutions of the required concentration were then prepared by dilution.

Apparatus and procedure

"Heterometric" titrations were carried out using a "Heterometer" constructed by M. Bobtelsky for the study of reactions in a heterogeneous system. A description of the heterometer and the procedure involved in heterometric titrations has been given in previous papers[6-9]. Two series of titrations were made, one by adding thorium to a solution of tartrate, and another, the reverse titration of a solution of thorium with tartrate. pH and conductivity titrations (at $25 \pm 0.1°C$) were carried out parallel to the heterometric titrations. All heterometric and pH titrations were carried out at room temperature (18-27°).

RESULTS

Heterometric titrations

Figure 1 shows the composition and results of three titrations of solutions of thorium nitrate with sodium tartrate. Curves 1 and 2 are plots of the results of titrations carried out with an initial volume of 20 ml and in an absorption cell of larger diameter than that used in the titration plotted in curve 3 which was carried out with an initial volume of 10 ml. Therefore, the values for the optical densities obtained in curve 3 differ greatly from those obtained in curves 1 and 2. Curves 1 and 2 show identical results. On the gradual addition of tartrate to a solution of thorium, a clear solution is obtained at first. The point on the abscissa corresponding to the initial precipitation lies at the molar ratio 1 [Th] : 1 [Ta] (Ta = tartrate anion). On the addition of about 10—20% tartrate beyond this point, the maximum density is reached (supersaturation?). The point of complete redissolving is obtained at the molar ratio 1[Th]: 2[Ta] by extrapolation, (The redissolving of the last particles of the precipitate is obtained only on the addition of an excess of sodium tartrate.) In curve 3, the concentration of thorium is almost doubled, and hence, the maximum density is much higher than in curves 1 and 2. The results are identical with those of curves 1 and 2. The composition

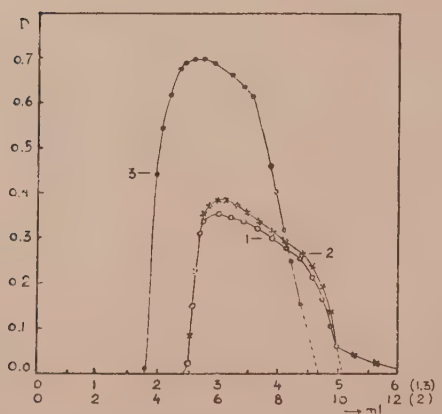

Figure 1
1. 5cc 0.1M $Th(NO_3)_4$+15cc H_2O+xcc 0.2M Na_2Ta
2. 5cc 0.1M $Th(NO_3)_4$+15cc H_2O+xcc 0.1M Na_2Ta
3. 4cc 0.1M $Th(NO_3)_4$+ 6cc H_2O+xcc 0.2M Na_2Ta

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and the results of the reverse titrations are shown in Figure 2 (curves 1—3). The experiments were carried out both with sodium and with potassium tartrate solutions for the purpose of comparison. Identical results were obtained. Curves 1 and 2 show that the point on the abscissa of a sudden precipitation lies at the molar ratio of approximately 1 [Th] : 2 [Ta] (= $[ThTa_2]$). The influence of an excess of thorium on the precipitate was studied (curve 3). The maximum density point is reached at a molar ratio of 1 [Th]: 1 [Ta] ($[ThTa]_n \downarrow$). An excess of thorium dissolves the precipitate at the approximate ratio 1 [Ta] : 2 [Th] (= $[Th_2Ta] \uparrow$).

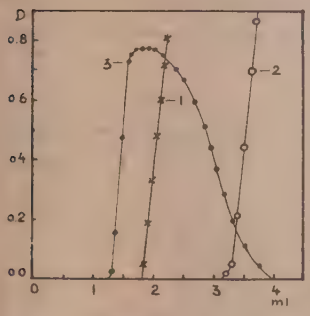


Figure 2

1. 3cc 0.1M K_2Ta+7cc H_2O+xcc 0.1M $Th(NO_3)_4$
2. 6cc 0.1M Na_2Ta+4cc H_2O+ xcc 0.1M $Th(NO_3)_4$
3. 2cc 0.1M K_2Ta+8cc H_2O+xcc 0.1M $Th(NO_3)_4$

Summarizing, the above phenomena may be explained as follows, In water solution two soluble complexes are obtained: one, $[ThTa_2]$, on the addition of excess tartrate, and the other, $[Th_2Ta]$, on the addition of excess thorium. In addition, a difficultly soluble salt of the empirical composition $[ThTa]_n \downarrow$ is formed. The real structure of the latter is probably Th $[ThTa_2]$ or $[ThTa]_2$. Figs 3 and 4 show the result of analogous titrations carried out in 50% alcoholic solution. Both sodium tartrate and potassium tartrate were used for comparison. In both titrations (Figure 3) the precipitation begins before the ratio of 1 [Th] : 1 [Ta] is reached in solution. The density increases abruptly and the maximum is reached at the molar ratio of approximately 1 [Th] : 1 [Ta]. It is interesting to note that an excess of potassium tartrate has no dissolving effect on the precipitate. (It is possible that the salt K_n $[ThTa_2]$ which would be obtained on the addition of an excess of tartrate is also insoluble). An analogous experiment with sodium tartrate could not be made as the solubility of sodium tartrate in 50% alcohol is insufficient. Figure 4 shows results of three reverse titrations. Exp. 3 was carried out in a cell of smaller diameter than that used in Exps. 1 and 2, to obtain a complete redissolving of the precipitate with a smaller amount of titrating solution. The curves obtained are of special interest as they give information concerning the various reactions which occur in the solid state as well as in solution. In general, the shape of the curves is similar. The curves show that the solubility of the tartrate complex ($Na_n[Th\ Ta_2]$?) which

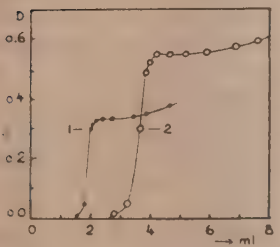


Figure 3

1. 2cc 0.1 M $Th(NO_3)_4$ + 3cc H_2O + 5cc alc. + xcc 0. 1 M K_2 Ta 50% alc.
2. 4cc 0.1M $Th(NO_3)_4$ + 1cc H_2O + 5cc alc. + xcc 0. 1 M K_2 Ta 50% alc.

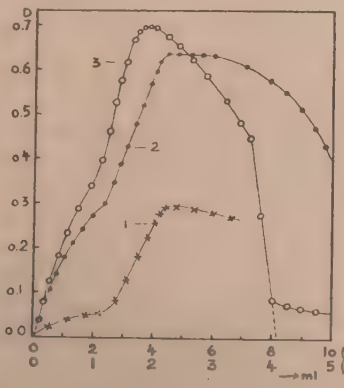


Figure 4

1. 5cc 0.05M Na_2Ta+5cc H_2O+10cc alc.+xcc 0.05M $Th(NO_3)_4$ 50% alc.
2. 5cc 0.1M Na_2Ta + 5cc H_2O+10cc alc. + xcc 0.1M $Th(NO_3)_4$ 50% alc.
3. 2cc 0.1M K_2Ta+3cc H_2O+5cc alc. + xcc 0.1 M $Th(NO_3)_4$ 50% alc.

precipitates at first is very limited. There is a break in the curve at the point of the quantitative formation of this salt. On further addition of thorium the direction of the curve changes and the density rises linearly and steeply. Approximately at the point of the maximum optical density the salt is transformed quantitatively into the insoluble salt Th $[Th\ Ta_2]$ or $[Th\ Ta]_2$. On addition of excess thorium, the maximum

value remains unchanged at first, and then decreases considerably. In curve 3 the complete redissolving of the salt $[Th\ Ta]_2$ can be observed at the molar ratio of 2 [Th] : 1 [Ta] ($=[Th_2Ta]$). (This result must be obtained by extrapolation since the slow dissolving of the last grains of the precipitate interferes.)

In order to study the behaviour of thorium tartrate on addition of alkali, some heterometric titrations were carried out in the presence of sodium hydroxide. The composition of the experiments and the results obtained are shown in Figure 5 (curves 1—5). In addition, curve 6 shows a titration with

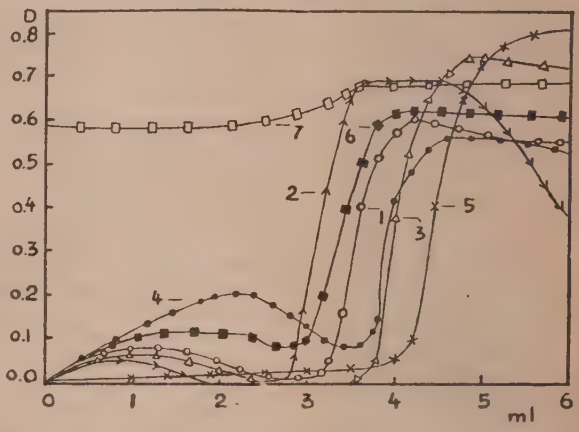


Figure 5

1. 4cc 0.1M Na_2Ta+3cc 0.2M NaOH + 13cc H_2O+0.1M $Th(NO_3)_4$
2. 4cc 0.1M Na_2Ta+ 2cc 0.2M NaOH +14cc H_2O+xcc 0.1M $Th(NO_3)_4$
3. 5cc 0.1M Na_2Ta+3cc 0.2M NaOH + 12cc H_2O+xcc 0.1M $Th(NO_3)_4$
4. 4cc 0.1M Na_2Ta+8cc 0.1M NaOH +8cc H_2O+xcc 0.1M $Th(NO_3)_4$
5. 6cc 0.1M Na_2Ta+4cc 0.1M NaOH + 10cc H_2O+xcc 0.1M $Th(NO_3)_4$
6. 4cc 0.1M Na_2Ta+3cc 1M NH_4NO_3+ 3cc 0.2M NaOH+ 10cc H_2O+xcc 0.1 M $Th(NO_3)_4$
7. 4cc 0.1M Na_2Ta+4.1cc 0.1M Th $(NO_3)_4$ +11.9cc H_2O+ xcc 0.2M NaOH

ammonia instead of sodium hydroxide for comparison. If we compare curve 1 with curve 6, we see that we obtain almost the same effect with ammonia as with sodium hydroxide. Almost all the curves (1—6) show in the first part of the titration small density values which rise on the addition of thorium until a maximum of a relatively low optical density value is obtained, and then the optical densities decrease practically to zero values. On further addition of thorium, a point of initial precipitation is obtained, following which the optical density rises steeply, until a maximum point is reached. At this point, the optical density either remains constant or begins to decrease slowly. The small densities resulting in the low maxima obtained in the beginning may be caused by a compound which is formed at first, and which may afterwards either be dissolved or transformed into a soluble complex. As Figure 5, curve 7, shows, the insoluble $[ThTa]_2$, once precipitated, is no longer soluble on addition of sodium hydroxide (but is fairly soluble in dilute hydrochloric acid).

We may assume that in the presence of sodium hydroxide, soluble complexes are obtained between thorium and tartrate by neutralization of one ($=Ta'$) or both hydroxy groups ($=Ta''$) of the tartrate anion, resulting in groups which have a valency of *three* ($=Ta'$) or *four* ($=Ta''$). As soon as the sodium hydroxide is used up for this purpose, the remaining free Ta^{2-} anion (if any is left in solution) reacts with an excess of thorium according to the following equations:

$$Th + 2Ta \rightleftarrows [ThTa_2] \uparrow$$

$$Th + [ThTa_2] \longrightarrow [ThTa]_2 \downarrow$$

The results obtained from curves 1—5 of Figures 5 are compiled in Table 1. Calculations were made under the assumption that the sodium hydroxide is at first used up quantitatively for the formation of Ta′ or Ta″, and that the reactions given above then take place quantitatively in solution. The calculated values which are in closest agreement with the measured values are underlined in the table. If we compare the values of columns 4, 11, and 12 we see that the only assumption which conforms well with the experimental results is that in a solution containing sodium hydroxide a mixture of two complex compounds, namely [ThTa″] and [ThTa′Ta] or $[ThTa_2]$ are formed. The assumption that a complex compound [ThTa′] exists in solution side by side with [ThTa″] (*cf.* columns 4 and 14) does not conform with the results obtained. As to the additional amount of thorium required to precipi-

tate the soluble complexes as insoluble thorium salts (*cf.* columns 6 and 15), we see that probably only the complex $[ThTa_2]$ is precipitated by the excess of thorium.

TABLE

General Composition: acc 0.1 M Na_2Ta + bcc 0.1 M NaOH + (20-a-b) cc H_2O + X cc 0.1 M $Th(NO_3)_4$

Curve No. (1)	NaOH (cc) (2)	Na_2Ta (cc) (3)	cc thorium measured: At beginning of precip. (4)	cc thorium measured: At end of precip. (5)	△ (6)	cc soluble thorium calculated as: $ThTa_2$ or $ThTa'_2$ (7)	$Th\text{-}Ta''$ (8)	$Th\text{-}Ta'$ (9)	Th_2Ta'' (10)	$ThTa'' + ThTa_2$ (11)	$ThTa'' + ThTa'Ta$ (12)	$ThTa'' + ThTa'_2$ (13)	$ThTa' + ThTa''$ (14)	cc thorium required for precip. of: $ThTa'' + ThTa_2$ (15)
1	6	4	3.3	4.1	0.8	2.0	3.0	—	6.0	3+0.5 =3.5	2.66+0.66 =3.3	2+1=3	2+254	0.5
2	4	4	2.8	3.8	1.0	2.0	2.0	4.0	4.0	2+1 =3	1.33+1.33 =2.7	0+2=2	4+0=4	1.0
3	6	5	3.8	4.8	1.0	2.5	3.0	—	6.0	3+1 =4	2.33+1.33 =3.7	1+2=3	4+1=5	1.0
4	8	4	3.8	4.6	0.8	2.0	4.0	—	8.0	4+0 =4	4+0=4	4+0=4	0+4=4	0.0
5	4	6	4.0	5.6	1.6	3.0	2.0	4.0	4.0	2+2 =4	0.66+2.66 =3.3			2.0

pH Titrations

The study of thorium solutions by means of pH measurements especially at low pH is very restricted as the thorium nitrate solution itself has a pH ~ 3. Figure 6 presents the results of two pH titrations.

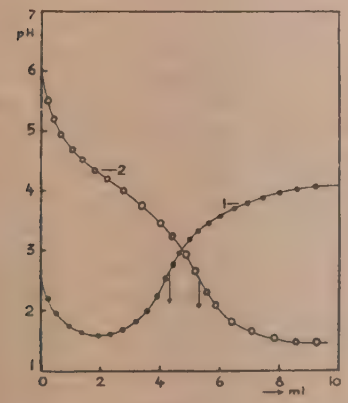


Figure 6

1. 4cc 0.1M $Th(NO_3)_4$+16cc H_2O+xcc 0.2M Na_2Ta
2. 12cc 0.1M Na_2Ta+8cc H_2O+xcc 0.1M $Th(NO_3)_4$

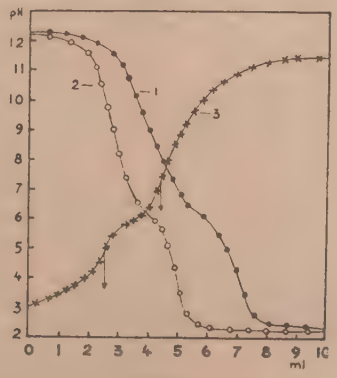


Figure 7

1. 8cc 0.1M Na_2Ta+6cc 0.2M NaOH+6ccH_2O +xcc 0.1 M $Th(NO_3)_4$
2. 6cc 0.1M Na_2Ta+4cc 0.2M NaOH+10cc H_2O +xcc 0.1M $Th(NO_3)_4$
3. 10cc 0.1M Na_2Ta+4cc 0.1M $Th(NO_3)_4$+6cc H_2O+ xcc 0.2M NaOH

Here (as in the case of citrate) the pH falls on addition of sodium tartrate to a solution of thorium nitrate (curve 1) from pH ~ 3.0 to pH ~ 1.6. The lowest values are obtained on the complete formation of the insoluble $[ThTa]_2\downarrow$. On further addition of sodium tartrate and on the formation of $[ThTa_2]\uparrow$ the pH rises. The point of inflection (pH ~ 2.7) occurs at the molar ratio of 1 [Th]: 2 [Ta] (= $[ThTa_2]$)*; the point of inflection (pH ~ 2.7) is obtained at the point of the complete formation of $[ThTa_2]$.

* In the reverse titration (curve 2)

Figure 7 shows the results of three pH titrations carried out in the presence of sodium hudroxide. In curves 1 and 2, the upper inflection point cannot be determined with accuracy. The second inflection point occurs at pH 4—5, at the beginning of the precipitation of an insoluble thorium salt. Curve 3 shows the result of a titration of a solution containing the complex $[ThTa_2]$ with sodium hydroxide. The solution remains clear throughout the titration. Two inflection points are obtained; the first, at pH $\sim$ 5.0, occurs when approximately one equivalent of sodium hydroxide has been added per one thorium and the second, at pH$\sim$7.5, occurs on addition of two equivalents of alkali. This suggests that the neutralization of the complex $[ThTa_2]$ occurs in two stages.

Conductometric titrations

Two conductometric titrations were carried out and the results plotted in Figure 8. On the addition of thorium to a tartrate solution (curve 1) there is no marked change in the conductivity until the precipitation of $[ThTa]_2\downarrow$ is complete. On further addition of thorium the conductivity rises rapidly and a break in the curve occurs at the molar ratio of <2 [Th] : [Ta]. In the reverse titration (curve 2) the conductivity increases rapidly and linearly until the precipitation of the $[ThTa]_2$ is complete (the possibility of a partial solution of $[ThTa]_2$ must be considered), at which point the maximum conductivity is obtained. On further addition of tartrate, the conductivity falls rapidly and linearly, and a minimum is reached at the molar ratio of approximately 1 [Th] : 2 [Ta]. On continued addition of tartrate, the conductivity again increases. Although curve 2 confirms the presence of the two compounds [ThTa] and $[ThTa_2]$ it is not easy to explain all the conductivity changes observed.

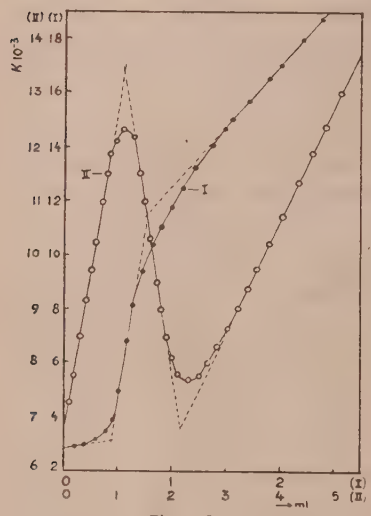


Figure 8

1. 5cc 0.1M Na_2Ta+45cc H_2O+xcc 0.5M $Th(NO_3)_4$
2. 5cc 0.1M $Th(NO_3)_4$+45cc H_2O+xcc 0.5M Na_2Ta

DISCUSSION

The following discussion would be very complicated if ionic charges were used in the presentation of the various complexes detected by measurements. We therefore will present formulas based on the molar ratios of the components without consideration of their ionic charges. The phenomena observed may be accounted for as follows: We assume that two *unstable* "primary groups" $ThTa_4$ and Th_4Ta are formed under extreme conditions, $ThTa_4$ is formed in solutions which contain large excesses of tartrate and only traces of Th^{IV} while Th_4Ta is formed in solutions of thorium which contain traces of Ta. As the coordination number of Th^{IV} and Ta are both equal to four, we obtain Th_4Ta or $ThTa_4$. The subsequent reactions are as follows:

$$(1)\quad ThTa_4 + Th \rightleftarrows [ThTa_2]\uparrow$$

$$(2)\quad ThTa_2 + Th \rightleftarrows Th\,[ThTa_2]\downarrow \text{ or } [ThTa]_2\downarrow$$

$$(3)\quad Th_4Ta + Ta \rightleftarrows [Th_2\,Ta]\uparrow$$

$$(4)\quad Th_2Ta + Ta \rightleftarrows Th\,[ThTa_2]\downarrow \text{ or } [ThTa]_2\downarrow$$

$$(5)\quad [ThTa]_2 + 2\,Ta \rightleftarrows 2\,[ThTa_2]\uparrow$$

The existence of the products of all five reactions are confirmed by measurements. The soluble $[ThTa_2]$ reacts as if it were an anion which forms salts with cations. The alkali salts are soluble in water but more difficulty soluble in 50% alcohol. In solutions containing a sufficient quantity of sodium hydroxide, the following reaction occurs quantitatively:

$$(6)\quad Ta + 2OH^- + Th \rightleftarrows [ThTa''']^o + 2H_2O$$

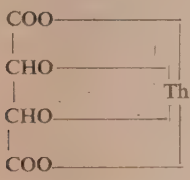
$[ThTa'']^{o}$ is quantitatively formed in solutions of pH ~ 8 (or higher). At lower pH's the complexes $[ThTa'Ta]$ and $[ThTa_2]$ exist in solution (see (7) and (8) below) side by side with the insoluble $[ThTa]_2\downarrow$.

As we see, there are two different compounds of the same molar ratio 1 [Th] : 1 [Ta] ; one is insoluble and exists even at a low pH (~ 2.0), while the other is soluble and exists only in alkaline solution. If there is an excess of sodium tartrate relative to sodium hydroxide in the solution, then on addition of thorium, the insoluble $[ThTa]_2$ is obtained which exists side by side with the soluble $[ThTa'']^{o}$. The insoluble $[ThTa]_2\downarrow$ is formed quantitatively by addition of thorium to a solution which contains the complex $[ThTa_2]$ according to (2) and again dissolves in an excess of tartrate according to (5). Although $[ThTa]_2$ is easily soluble in an excess of tartrate, this compound, as experiment shows, once precipitated is no longer easily soluble on addition of sodium hydroxide.

The presentation of the reactions which occur on addition of thorium to solutions containing both tartrate and sodium hydroxide in a molar ratio of 1 Ta : $<$ 2 NaOH is more complicated. In this case, in addition to $[ThTa'']^{o}$, the complexes $[ThTa_2]$ or $[ThTa'Ta]$ are formed. However, neither $[ThTa']$ (or $[ThTa']_n$) nor $[ThTa'_2]$ appear to be present in solution.

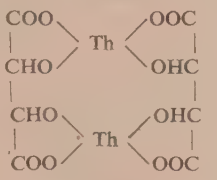
From the above, the following conclusions may be drawn about the existence and structures of the compounds obtained: $[ThTa'']^{o}$ may be presented either as a monomer or a dimer:

I



or

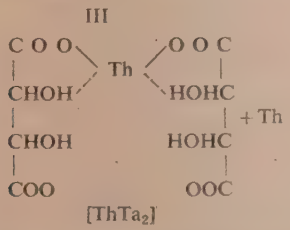
II



$([ThTa'']^{o}_2)$

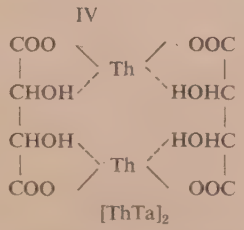
The structure of the other complexes may be presented as follows, taking into consideration the pH of the solution.

III



$[ThTa_2]$

IV



$[ThTa]_2$

In addition to $[ThTa_2]$ a soluble complex $[ThTa'Ta]$ may exist at somewhat higher pH according to the following equation:

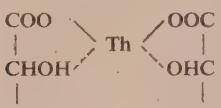
$$(7)\quad [ThTa_2] \underset{pH\sim 3}{\overset{pH\sim 5}{\rightleftharpoons}} [ThTa'Ta] + H^{+}$$

At pH~ 8 or higher, $[ThTa'']^{o}$ is quantitatively obtained according to the following reaction:

$$(8)\quad [ThTa'Ta] \underset{pH\sim 5}{\overset{pH\sim 8}{\rightleftharpoons}} [ThTa'']^{o} + Ta^{2} + H^{+}$$

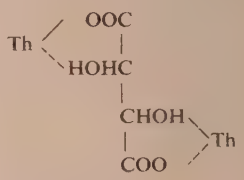
The structure of [ThTa′Ta] and [Th_2Ta] may be presented as follows:

V.



[ThTa′Ta]

VI.



[Th_2Ta]

REFERENCES

1. Bobtelsky, M. and Graus, B., 1953, *J. Amer. Chem. Soc.*, in press.
2. Britton, H. T. S., 1934, *Conductometric Analysis*, Chapman and Hall, London, p. 153.
3. Gebauer, R., 1943, *C.A.*, **37**, 5081p.
4. Gebauer, R., 1944, *C.A.*, **38**, 378.
5. Haissinsky, M. and Jeng-Tsong, Y., 1949, *Anal. Chim. Acta*, **3**, 422.
6. Bobtelsky, M. and Graus, B., 1953. *J. Amer. Chem. Soc* 4172
7. Bobtelsky, M. and Graus, B., 1953, *Analytica chimica Acta*, **9**,163
8. Bobtelsky, M. and Bargadda, 1953, *Bull. de Soc. Chim.* 276; *ibid.*, 382.
9. Bobtelsky, M. and Bargadda, I, 1953. *Analytica chimica Acta*, **9**,168.

THE THERMAL DECOMPOSITION OF GUANIDINE PERCHLORATE PART II. KINETICS

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In a previous communication[1], the following mechanism for the thermal decomposition of guanidine has been proposed on the basis of the analysis of the reaction products identified under varying conditions:

1) $CH_5N_3.HClO_4 \rightleftharpoons CN.NH_2 + NH_4ClO_4$

1a) $NH_4ClO_4 \rightleftharpoons NH_3 + HClO_4$

2) $3\ CN.NH_2 \longrightarrow C_3H_6N_6$ (melanine)

3) $C_3H_6N_6 + HClO_4$ (or NH_4ClO_4) $\longrightarrow$ HCl, CO, CO_2, N_2, NH_3, O_2, H_2O.

This mechanism has now been substantiated by kinetic measurements in the temperature range of 345—380°: the quantity of gas, expressed in % of the total gas evolved in each experiment, was determined as a function of the reaction time: the total amount of gas was 90—94% of the quantity theoretically expected throughout.

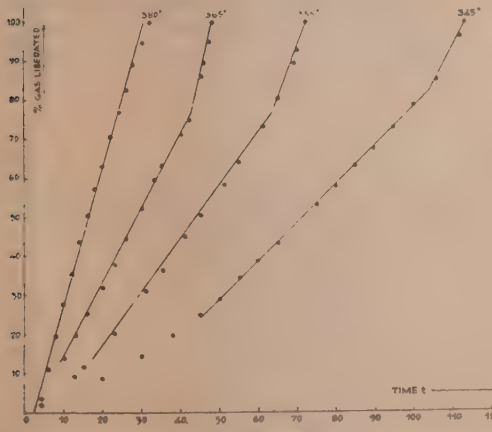

Figure 1
Thermal decomposition of guanidine perchlorate at different temperatures

The curves so obtained (Figure 1) consist of three sections: In the first section, the rate of gas formation increases, up to a constant value; in the second section (15—80% of the total gas), the rate remains constant; in the third it rises to a high value which resembles the rate of an explosion. The second, linear, section which corresponds to the main reaction, is of zero order. In Table I, the rate of gas evolution in this section of the curve is recorded for four different temperatures.

The dependence of the rate constant K on the temperature is expressed by the following equation:

(4) $k = 2.4 \times 10^{11}\, e^{-32,400/RT}$ %/min.

In accordance with the postulated mechanism, equimolar mixtures of ammonium perchlorate and dicyandiamide or of ammonium perchlorate and guanidine chloride give similar curves (Figure 2) and reaction rates (Table II); this proves that reaction (1) above cannot be the rate determining step.

Potassium perchlorate, on the other hand, oxidises dicyandiamide or guanidine chloride much more slowly (Figure 2).

TABLE I
Thermal decomposition of guanidine perchlorate

Temperature (°C)	*K* (% *per min.*)
345	0.95
355	1.35
365	1.95
380	3.6

TABLE II
Thermal decomposition of a mixture of ammonium perchlorate and guanidine chloride

Temperature (°C)	*K* (% *per min.*)
355	1.6
365	2.33

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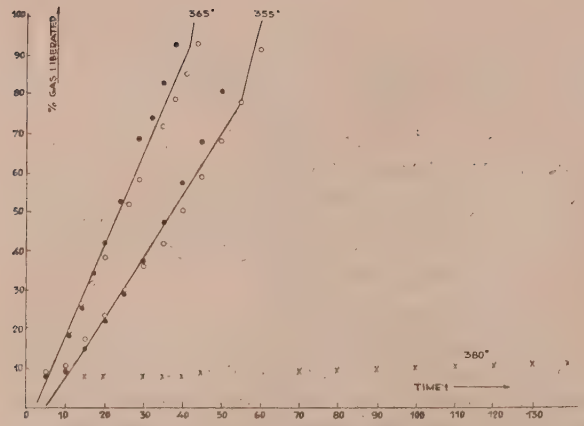

Figure 2

Thermal decomposition of mixtures of — guanidine chloride and ammonium perchlorate (O) dicyandiamide and ammonium perchlorate (●) guanidine chloride and potassium perchlorate (X)

As potassium perchlorate dissolves easily in molten guanidine chloride, this lowered reactivity cannot be due to physical causes, but tends to indicate that not the perchlorate ion is the oxidising species, but the free perchloric acid which is set free from ammonium perchlorate (1a), in a reaction which may, *e.g.*, take place on the walls of the vessel, and the rate of which may depend, therefore, only upon the area of contact between the ammonium perchlorate and the wall.

For the rate of the oxidation, as measured by the volume (v) of permanent gases evolved, we may write, in accordance with (3), generally

$$(5) \quad dv/dt = k_3(C_3H_6N_6)^m\ (HClO_4)^n$$

If a stationary state of the concentrartion of perchloric acid is assumed during the main reaction, one obtains

$$(6) \quad d[HClO_4]/dt = k_1 - k_3(C_3H_6N_6)^m(HClO_4)^n = 0$$

where k_1 = rate of the dissociation of the perchlorate according to (1a). Hence

$$(7) \quad k_1 = k_3[C_3H_6N_6]^m\,[HClO_4]^n$$

and

$$(8) \quad dv/dt = k_1.$$

The overall reaction rate appears thus to be a simple function of the speed with which free perchloric acid is formed. The slowness of the decomposition reaction in the first step of the reaction can then be ascribed to the absence of ammonium perchlorate and, therefore, of the free acid at this stage, *i.e.*, to the relative slowness with which guanidine perchlorate decomposes (1). Indeed, addition of ammonium perchlorate suppresses this induction period.

As to the third, very fast, step in the decomposition reaction, it has its counterpart in the thermal decomposition of nitrogen trichloride[2] which is also a reaction of zero order. The theory has been advanced that the first step in this reaction is the formation of $[NCl_2)$ and that $[NCl_2][NCl_3] = \text{constant}$. Towards the end of the reaction, when $[NCl_3]$ is small, the concentration of the $[NCl_2]$ increases and explosion occurs. Analogously, one can assume that the explosive step in the decomposition of guanidine perchlorate is due to gradual accumulation of perchloric acid, parallel with the decrease in the quantity of organic matter present.

REFERENCES

1. Glasner and Makovky, 1953, *J. Chem. Soc.*, 182. 2. Griffiths and Norrish, 1932, *Proc. Roy. Soc.*, **130**, 591; **135**, 69.

A TOTAL SYNTHESIS OF PYRENE*

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A number of reactions is known in which pyrene (I) has been obtained from suitably substituted biphenyl or phenanthrene derivatives; however, the yields reported are extremely low. This is true of the pyrolysis of 2,6,2',6'-tetramethylbiphenyl (II)[1] or 2,2'-diethylbiphenyl (III)[2], of the formation of pyrene from ethylene and phenanthrene (0.04% yield)[1,2] and of the pyrene synthesis from biphenyl-2,6-diacetic acid (IV)[3]. Also the formation of pyrene by zinc dust distillation of phenanthrene-4-aldehyde-5-carboxylic acid (V)[4] cannot be considered as a true total synthesis of the hydrocarbon, since (V) can be obtained only from pyrene by oxidative degradation.

The phenanthrene synthesis from 2,2'-bis-bromomethyl-biphenyl derivatives and lithium phenyl[5-10] appeared to offer an easy route into the pyrene series, if it were possible to apply the reaction to 2,6,2',6'-tetra-(bromomethyl)- biphenyl (VII). This substance could be prepared in 90% yield by bromination of 2,2'-bis-(bromomethyl)-6,6'-dimethyl-biphenyl (VI) with *N*-bromosuccinimide. Its treatment with lithium phenyl gave, indeed, in a yield of 30% the expected 1,2,6,7-tetrahydropyrene (VIII) which Coulson[11] had obtained by catalytic hydrogenation of pyrene (I) and which he has been able to dehydrogenate to pyrene. Its exact structure follows from the oxidative degradation to biphenyl - 2, 6, 2',6'-tetracarboxylic acid[11]. In addition to (VIII), a considerable amount of polymeric material was obtained, obviously by intermolecular reaction of (VII) with lithium phenyl; similar observations have been made in the analogous case of 2,2'-bis-(bromomethyl)-diphenylmethane and-dibenzyl[10].

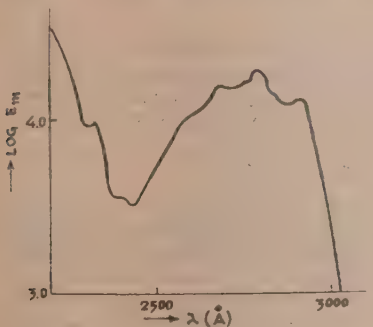
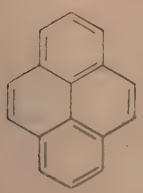


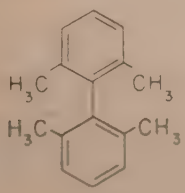
Figure 1.

U. V. Spectrum of tetrahydropyrene (VIII) in alcoholic solution

The spectrum of tetrahydropyrene (VIII) has been studied (Figure 1). It consists of three bands (at 2690, 2795 and 2915Å) and is thus similar to that of methylene-dihydrophenanthrene (IX)[12] (2700 and 2850Å) and 2,4,6, 2',4',6'-hexamethyl-biphenyl (X)[13] (2680 and 2750 Å). The fact that the spectrum shifts towards the visible region if one passes from (X) via (IX) to (VIII) can be explained by the increasing planarity and strainlessness of the biphenyl system. In accordance with this explanation, 4,5-dimethyl-9,10-dihydro-phenanthrene (XI) which is considerably strained shows a significant absorption only at 2610A[9].



I



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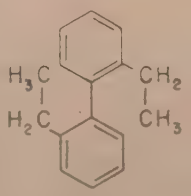

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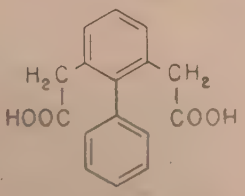

IV

* This investigation forms part of a thesis submitted by Zvi Pelchowicz to The Hebrew University of Jerusalem in partial fulfilment of the requirements for the degree of Ph.D.

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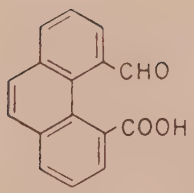

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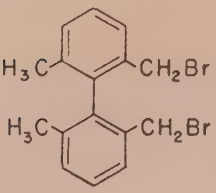

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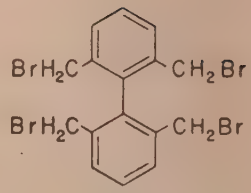
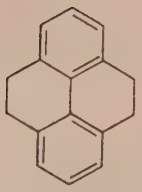
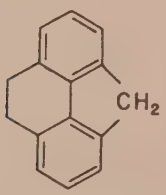


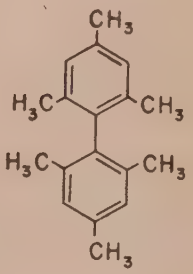
VII



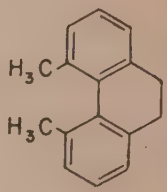
VIII



IX



X



XI

EXPERIMENTAL

2,2',6,6'-*Tetra*-(*bromomethyl*)-*biphenyl* (*VII*). A solution of 3 g of 2,2'-bis-(bromomethyl)-6,6'-dimethyl-biphenyl (VI)[10],3 g of *N*-bromo-succinimide and some benzoyl peroxide in 40 ml of carbon tetrachloride was refluxed for four hours, filtered and concentrated. The residue was triturated with petroleum ether, filtered and recrystallised from a mixture of petroleum ether and benzene. The compound formed elongated prisms, m.p. 167.5—168°; yield, 90%.

Anal. Calcd. for $C_{16}H_{14}Br_4$: Br, 60.8. Found: Br, 60.6;60.8.

1,2,6,7-*Tetrahydropyrene* (*VIII*). A solution of 3 g of the tetrabromo-compound in 200 ml of dry benzene was treated at 5—10° and with vigorous agitation with a solution of lithium phenyl (0.085 g of lithium, 1.9 g of bromobenzene and 25 ml of ether). The reaction product was agitated at room temperature for another two hours, decomposed with water and dilute sulfuric acid, and the organic layer washed with bicarbonate solution and water and dried. The solvent was evaporated and the residue treated with low-boiling petroleum ether which left 0.72 g(60%) of bromide-free, polymeric material undissolved. The petroleum ether was evaporated and the residue distilled evaporatively under 0.1 mm pressure (up to 150°). The distillate, which crystallised almost completely, was triturated with petroleum ether and melted at 138°, as indicated by Coulson[11]. Yield, 0.35 g (30%).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.2; H, 6.8. Found: C, 93.0; H, 6.8.

REFERENCES

1. Mattson, G., 1905, Quoted by Elsevier, *Encyclopedia of Organic Compounds*, **145**, 408.
2. Quist, W., 1937, *Ann.*, **532**, 302.
3. Chatterjee, N. N., and Bose, A., 1941, *Chem. Abstr.*, **35**, 7960.
4. Vollmann, H., 1937, *Ann.* **531**, 35.
5. Hall, D. M., and Turner, E. E., 1949, *Nature*, **163**,537.
6. Hall, D. M., Lesslie, M. S. and Turner, E. E., 1950, *J. Chem. Soc.*, 711.
7. Hall, D. M. and Turner, E. E., 1951, *J. Chem. Soc.* 3072.
8. Bergmann, E. and Szmuszkovicz, J., 1951, *J. Amer. Chem. Soc.*, **73**, 5153.
9. Bergmann, E. and Pelchowicz, Z., 1953, *J. Amer. Chem. Soc.*, **75**, 2663; *J. Org. Chem.*, **18**, in press.
10. Bergmann, E. and Pelchowicz, Z., 1953, *J. Amer. Chem. Soc.*, **75**, 4281.
11. Coulson, E. A., 1937, *J. Chem. Soc.*, 1298.
12. Jones, N., 1941, *J. Amer. Chem. Soc.*, **63**, 1658.
13. Pickett, L. W., Walter, G. F. and France, H., 1936, *J. Amer. Chem. Soc.*, **58**, 2296.

SYNTHESES WITH CYCLOHEXEN-1-ALDEHYDE

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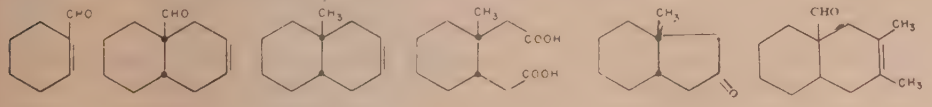
Cyclohexen-1-aldehyde (I) which has recently[1] become easily accessible, represents a type of α, β-unsaturated aldehyde which has not yet been studied as to its potentialities in organic syntheses. It should be useful as an acceptor in Michael reactions and as philodienic compound. Of particular interest appear to be Diels-Alder reactions with (I), as their products would contain an angular aldehyde group as it occurs in such natural products as strophanthidin and α-antiarin[2]. Some representative reactions of (I) have, therefore, been studied.

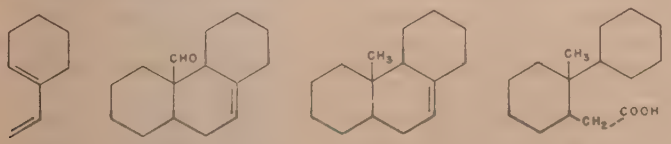
With butadiene, an adduct was formed which was characterised as its 2,4-dinitrophenylhydrazone and identified as *cis*-$\triangle^{2(3)}$-octalin-9-aldehyde (II) in the following unambiguous manner: Reduction according to the method of Huang-Minlon[3] gave a liquid hydrocarbon (presumably III), which could be oxidised according to Burnop and Linstead[4] to *cis*-1-methyl-cyclohexane-1,2-diacetic acid (IV) of m.p. 190° (the trans-isomer melts at 164°). For further identification, (IV) was cyclised by means of barium hydroxide to the known *cis*-8-methyl-2-hydrindanone (V)



I II III IV V VI

It is interesting that the spectrum of (II) is very similar to that of strophanthidin and α-antiarin for which $\lambda_{max} = 305$ and 303 mμ, log $E = 1.8$, has been reported. (II) in alcoholic solution has $\lambda_{max} = 292$ mμ, log $E = 2.2$.

2,3-Dimethylbutadiene gave with (I) an adduct, very probably (VI), which is characterised by its semicarbazone and its dinitrophenylhydrazone. Also with 1-vinyl-cyclohexene (VII) an adduct was obtained which analysed correctly for 1,2,3,4,5,6,7,8,9,4a,5a,8a-dodecahydrophenanthrene-5a-aldehyde (VIII)[6]. No semicarbazone or dinitrophenylhydrazone could be obtained, probably for steric reasons[7], but the following reactions make the structure (VIII) very probable. The compound is reduced by the



VII VIII IX X

method of Huang-Minlon[3] to a hydrocarbon for which the analysis indicates formula (IX). Its ozonization in glacial acetic acid as solvent gave a ketoacid which was not isolated but reduced directly to a well-crystallized acid $C_{15}H_{26}O_2$ which would have formula (X) of a (2-methyl-2-cyclohexyl-cyclohexyl)-acetic acid.

It has thus been shown that models for the strophanthidin structure can be built up by this method which offers a wide range of attractive applications for further investigations.

EXPERIMENTAL

Cyclohexen-1-aldehyde (I) was prepared according to Seifert and Schinz[1] from the 2-hydroxymethylene-derivative of cyclohexanone[8]. This derivative was converted into the enol ethyl ether by azeotropic

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distillation with ethanol and *p*-toluenesulphonic acid in presence of benzene (b.p. 100°/2 mm) and the enol ether reduced. From 156 g of the enol ether, 61 g of (I) was obtained. B.p. 75°/25 mm. The absorption spectrum (λ_{max} = 2310A; E=10,500) was in accord with the formula, and the semicarbazone (from dilute alcohol) had a m.p. (218—219.5°) conforming with the value (213—216°) reported by Plattner and Jampolski[9]. *Anal.* Calcd. for $C_8H_{13}N_3O$: C, 57.5; H, 7.8. Found: C, 57.8; H, 7.6.

Cis-$\triangle^{2(3)}$-*octalin*-9-*aldehyde* (II). Cyclohexene-1-aldehyde (9.5 g), butadiene (9.3 g) and hydroquinone (0.15 g) were heated at 180° for seventeen hours in a closed tube. Distillation gave 14.0 g of unchanged starting material, 1.5 g of (II), b.p. 115° (20 mm), and 2 g of polymeric residue. *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.5; H, 9.8. Found: C, 80.2; H,10.0.

The *dinitrophenylhydrazone* melted at 188—189°, after one recrystallisation from chloroform-ethanol. *Anal.* Calcd. for $C_{17}H_{20}N_4O_4$:C, 59.3; H, 5.9. Found: C, 59.3; H, 6.0.

Degradation

The Huang-Minlon reduction of (II) was carried out as usual, employing 1.5 g of the aldehyde, 2.24 g of potassium hydroxide, 14 ml of diethylene glycol and 3.9 ml of hydrazine hydrate. The crude pale-brown oil obtained was oxidised according to Burnop and Linstead[4], and the acidic material (IV) formed (m.p. 185—187°) recrystallised from dilute acetic acid. It then melted at 189—190°(literature [4]: 190°).

The ketonisation with barium hydroxide was also carried out according to Burnop and Linstead[4]. The crude semicarbazone, leaflets from dilute alcohol, melted at 214—215°; the m.p. was unchanged by further recrystallisation (reported m.p. of the semicarbazone of 8-methyl-2-hydrindanone (V)[5]: 219°).

2,3-*Dimethyl*-$\triangle^{2(3)}$-*octalin*-9-*aldehyde* (VI). Cyclohyxene-1-aldehyde (I) (9.5 g), dimethylbutadiene (7.8 g) and hydroquinone (0.1 g) were heated at 180° for eighteen hours in a Pyrex tube. Distillation at 20 mm gave 6.0 g of starting material, 5 g (29%) of (VI), b.p. 144—147°, and 5.5 g of polymeric product. *Anal.* Calcd. for $C_{13}H_{20}O$: C, 81.3; H, 10.4. Found: C, 81.5; H, 10.6.

The *semicarbazone* was prepared with semicarbazide acetate in dilute ethanol. After standing for one day, the clear solution was evaporated in a stream of air until crystals appeared. These were washed with a little ethanol and melted at 155—160°. Two recrystallisations from ethanol afforded plates, m.p. 161—163°. *Anal.* Calcd. for $C_{14}H_{23}N_3O$: C, 68.5; H, 9.4. Found: C, 67.8; H, 9.5.

The *dinitrophenylhydrazone* formed orange needles, which melted at 200—202°, after one recrystallisation from chloroform-ethanol. *Anal.* Calcd. for $C_{19}H_{24}N_4O_4$: C, 61.3; H, 6.4. Found: C, 61.6; H, 6.3.

1-*Vinyl-cyclohexene* (VII). 1-Ethynyl-cyclohexanol[10] was dehydrated to 1-ethynyl-cyclohexene by means of thionyl chloride and pyridine [11] and the acetylenic bond half-hydrogenated. A quantity of 18 g of the hydrocarbon in 50 ml of anhydrous alcohol required eighty-five minutes for the absorption of 1.1 mole of hydrogen, when the hydrogenation was carried out at room temperature and atmospheric pressure, using 0.3 g of 2% palladium-calcium carbonate as catalyst. B.p. 50—52°/22mm. The purity of the material was ascertained by its ultraviolet spectrum[11]: λ_{max} = 2300A; E = 18,000.

1,2,3,4,5,6,7,8,9,4a,5a,8a-*Dodecahydrophenanthrene*-5a-*aldehyde* (VIII). A mixture of 9 g of cyclohexen-1-aldehyde (I), 9 g of 1-vinyl-cyclohexene (VII) and 0.1 g of hydroquinone was heated at 180° for 17 hours. Distillation gave 7 g of starting material (b.p. 50—65°/20 mm), 9.5 g (53%) of (VIII), b.p. 120°/0.8 mm, n_D^{19} = 1.529, and 1 g of polymeric material. *Anal.* Calcd. for $C_{15}H_{22}O$: C, 82.5; H, 10.0. Found: C, 82.9; H, 10.4.

5a-*Methyl*-1,2,3,4,5,6,7,8,9,4a,5a,8a-*dodecahydrophenanthrene* (IX). A mixture of the aldehyde (VIII) (4.7 g), potassium hydroxide (4.85 g), hydrazine hydrate (64%) (8.5 ml) and diethylene glycol (31 ml) was refluxed for four hours. The internal temperature was then raised to 195° and the refluxing continued for 4.5 hours. The usual work-up afforded an oil, b.p. 105—107° (0.8 mm); yield, 4.0g. n_D^{24} = 1.516. *Anal.* Calcd. for $C_{15}H_{24}$: C, 88.2; H, 11.8. Found: C, 88.1; H, 11.6.

(2-*Methyl*-2-*cyclohexyl*-*cyclohexyl*)-*acetic acid* (X). The unsaturated hydrocarbon (IX) (3.5 g) was dissolved in 65 ml of glacial acetic acid and ozonised for four hours (5 l/h; 4% ozone) until the tetranitromethane test for double bonds was negative, Then 11 ml of 30% hydrogen peroxide was added and the solution heated for two hours on the steam-bath. It was evaporated *in vacuo*, and the residue dissolved in ether, washed with water, with acidified ferrous sulfate solution, and again with water, and

extracted with soduim hydroxide solution. Acidification gave an oil, which was isolated by extraction with ether, but could not be induced to crystallisation. Yield, 2.4 g. This keto-acid (2 g) was reduced (2.24 g of potassium hydroxide; 4.0 ml of 64% hydrazine hydrate, 12 ml of diethylene glycol; 1.5 hours refluxing, then heating for 4 hours at 195°). A brown oil was obtained (1.1 g) which crystallised spontaneously upon standing. After two days, the compound was recrystallised from acetone-water; it formed plates, m.p. 147—152°. One further recrystallisation from the same solvent mixture raised the m.p. to 165—166°, which remained unchanged on further recrystallisation. *Anal.* Calcd. for $C_{15}H_{26}O_2$: C, 75.6; H, 10.9. Found: C, 75.6; H, 10.9.

REFERENCES

1. SEIFERT and SCHINZ, 1951, *Helv. Chim. Acta*, **34**, 728.
2. TSCHESCHE and HAUPT, 1936, *Ber.*, **69**, 1377. *Cf.* also the recent paper by Tschesche and Petersen, 1953, *Ber.* **86**, 574.
3. HUANG-MINLON, 1946, *J. Amer. Chem. Soc.*, **68**, 2487.
4. ELSEVIER, *Encyclopedia of Organic Compounds*, **12B**, 107—108.
5. BURNOP and LINSTEAD, 1940, *J. Chem. Soc.*, 720.
6. A similar structure has been assigned recently to the adduct from 1-vinyl-cyclohexene (VII) and 2-cyclohexen-1-one (NAZAROV, TORGOV and KUVARZINA, 1952, *Chem. Abstr.*, **46**, 11122.
7. The aldehyde group in strophanthidin does not reduce Fehling's solution, but gives an oxime (JACOBS and COLLINS, 1925, *J. biol. Chem.*, **65**, 491; it has been reduced to methyl by Wolff-Kishner's method (PLATTNER, SEGRE and ERNST, 1947, *Helv. chim. Acta*, **30**, 1432.
8. JOHNSON and POSVIC, 1947, *J. Amer. Chem. Soc.*, **69**, 1361.
9. PLATTNER and JAMPOLSKI, 1943, *Helv. Chim. Acta*, **26**, 687.
10. Organic Syntheses, 1949, **29**, 47.
11. CHANLEY and SOBOTKA, 1949, *J. Amer. Chem. Soc.*, **71**, 4140.

CATION EXCHANGERS FROM OLIVE PITS

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INTRODUCTION

It is a known process to prepare cation exchangers by the action of sulphuric acid on carbonaceous materials such as coal, lignit, peat, agricultural wastes, etc. The reaction can be carried out with various agents such as SO_3 [1,2], concentrated sulphuric acid[2,3,4,5,6], fuming sulphuric acid[2], dilute sulphuric acid which is concentrated during the reaction[7], anhydrous $FeCl_3$[8], chlorosulphonic acid, as well as other sulphonating and oxidizing agents. It has been proposed that preliminary oxidation of the raw material for the exchanger be carried out with agents such as dichromates[9], permanganates, etc. This paper describes work done on the preparation of cation exchangers from olive pits by the action of concentrated sulphuric acid.

PREPARATION

The cation exchanger with the best exchange capacity is obtained in the following manner: 300 ml of concentrated sulphuric acid (Sp. gr. 1.82) are added with stirring to 150 g of ground olive pits (10—40 mesh) which had been previously dried at 160°—165°C. The reaction is exothermic. The mass is heated for one hour at 70°—80°C and for two hours at 170—180°C (Salt bath). The product is washed until the washings are no longer acid to litmus, then dried at 100°—110°C and screened.

The experimental work carried out to determine the exchangecapacity was done on the 20—40 U.S. mesh size fraction. Additional treatment with sodium carbonate or sodium hydroxide solutions as suggested by the literature did not improve the exchange capacity but instead caused excessive swelling of the exchanger and a tendency to colour the water, especially immediately after regeneration with salt solution and washing with distilled water.

DETERMINATION OF THE ACID GROUPS

The exchange capacity depends on the presence of acidic, mainly sulphonic (—SO_3H) and carboxylic (—COOH) groups[2]. In this particular case there is no suitable procedure available for the quantitative determination of the sulphonic groups. Therefore the assumption was made that all the sulphur in the exchanger was in the form of the sulphonic radical. Sulphur was determined by combustion in a calorimetric bomb. For comparison a commercial carbonaceous exchanger (Zeo—Karb) was also examined.

As to the carboxylic groups the methods described in the literature did not give reliable and reproducible results. Finally a procedure was adapted based on the work of Pfeiffer[10], who determined the equivalent weights of solid organic acids by reaction with gaseous ammonia. However, the equivalent acidic groups were determined not from the increase in weight, but from the amount of combined ammonia (Kjeldahl). It was assumed that the acid content above that represented by the sulphonic groups was due to carboxylic groups. From the results shown in Table I it is evident that the material prepared as described above did not undergo appreciable sulphonation, the sulphuric acid acting essentially as an oxidizing agent.

Therefore the exchange capacity is mainly due to the presence of carboxylic groups.

TABLE I
Amounts of Sulphonic and Carboxylic Groups

Sample	Total sulphur o/o	Total acidity meq/g	Sulphonic group* meq/g	Carboxylic group** meq/g
1	0.40	7.08	0.13	6.95
2	0.53	6.82	0.17	6.65
Zeo-Karb	4.58		1.43	

Note: Sulphur content of pits: 0.01%.
* Calculated from total sulphur.
** Difference between total acidity and that due to sulphonic groups.

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EXCHANGE CAPACITY

Hydrogen cycle

The exchange capacity was determined by a standard method[2,10], using small columns of about 20 mm diameter. The amount of softener used in each experiment was 25 ml, the regeneration being carried out by HCl of 15% or H_2SO_4 of 2% both giving the same efficiency. After regeneration the softener was washed with distilled water. Tap water of known hardness was passed through the softener until the hardness of the exit water rose to 15–20 p.p.m. ($CaCO_3$). In this way the working capacity of the sample was determined. The cycle was repeated for several times until the results remained constant.

Sodium cycle

The experiments described above were repeated for the sodium cycle. The regeneration was carried out with 8% NaCl solution.

Table II presents the results for three exchangers prepared from olive pits.

TABLE II
Exchange Capacity

Sample	Bulk density	Exchange Capacity H Cycle meq/ml	meq/g	kg $CaCO_3$/m³	Exchange Capacity Na Cycle meq/ml	meq/g	kg $CaCO_3$/m³
1	0.44	0.72	1.63	36.0	0.90	2.05	45.0
2	0.64	1.54	2.40	77.0	1.62	2.55	81.0
3	0.57	0.98	1.72	49.0	0.95	1.66	47.5
Zeo-Karb[12]		0.60	1.62				

Remarks

1) Hardness determination of the water before and after softening was done with Versene by the Schwarzenbach method[13].
2) The above olive pits which were used in the preparation of the exchanger displayed no softening properties.

CONCLUSION

a. The action of concentrated sulphuric acid on olive pits according to the procedure described, results essentially in oxidation, leading to carboxyl groups.

b. The results presented in Table II show that the exchange capacities of exchangers prepared from olive pits are comparable to the exchange capacity of commercial exchangers of the same type.

Note: An application for an Israel patent on this procedure has been submitted.

REFERENCES

1. Liebknecht, O., U.S.P. 2,191,059, Sept. 23, 1938.
2. Broderick, S. G. and Bogard Dale, 1941, *ind. Eng. Chem.*, 33, 1291.
3. Furness, R. and Grossfield, J. and Sons, Ltd., B.P. 455,374, Oct. 14, 1936.
4. Smit, P., U.S.P. 2,191,063, Jan. 10, 1935.
5. Liebknecht, U.S.P. 2,191,060, March 24, 1939.
6. United Water Softeners, Ltd., B.P. 450,574, July 21, 1936.
7. Riley, Ray, U.S.P. 2,170,065, Nov. 9, 1935.
8. Urbain, O. M. and Setemen, W. R., U.S.P. 2,294,764, July 10, 1939.
9. Carbonisation et charbons actifs, Ltd., F.P. 932,573, March 25, 1948.
10. Pfeiffer, P. and Hausen, R., 1931, *Journal J. Prak. Chemie* (2), 130, Nr. 1—3.
11. *Jour. of A.W.W.A.*, 1949, p. 455.
12. Cassidy, Harol James, Absorption and Chromatography, p. 269.
13. Dietil, Harvey, Goetz Charles A. and Hash, Clifford C., 1950, *Jour. A.W.W.A.*, 40—18

THE MEERWEIN REACTION OF β-NITROSTYRENE

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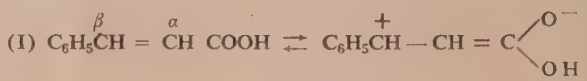
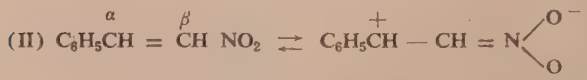
The olefinic bond of cinnamic acid possesses a characteristic polarity, due to the presence of two specific substituents: The carboxyl group, which is a strong electron-attractor, and the aromatic ring, which may serve as electron source or sink, thus enhancing the influence of the carboxyl on the olefinic double bond. Therefore the β-carbon atom of cinnamic acid appears as the positive end of the polarized form (I), and this specific electron distribution determines the behaviour of the molecule in ionic or radical additions to the double bond. Since the nitro group exerts a stronger electron-attracting influence than carboxyl, we decided to study the reactivity of the olefinic bond in β-nitrostyrene (II). It is known[1] that this compound adds aromatic hydrocarbons under the influence of Friedel-Krafts catalysts, although the final product is not analogous to the addition product of cinnamic acid. In this communication we represent preliminary results on the Meerwein reaction of β-nitrostyrene.

Aryldiazoacetates, in the presence of cupric chloride, attack cinnamic acid at the α-carbon, producing a stilbene derivative and—in addition—small amounts of a stilbene-carboxylic acid[2]. When we subjected β-nitrostyrene in acetone solution to the action of *p*-nitrophenyldiazo-acetate, no reaction occurred in the absence of cupric salt. In the presence of this catalyst, reaction took place, and two crystalline products could be isolated: 1) *p*-Nitrostilbene (III) and 2) a ketone of m.p. 112—114°, which according





to its analysis corresponds to either IVa or IVb. The first isomer is known[3]. Its m.p. (145°) and the m.p. of its 2,4-dinitrophenylhydrazone (233—234°) are different from our product. IVa gives a strong violet colour upon contact with cold ethanolic potassium hydroxide[4]. In contrast, our ketone produces a weak red-brown colour only after heating with this reagent, and its hydrazone melts at 239—240°. The non-identity of our product with the ketone IVa is also evident from a comparison of the absorption spectra (Figure 1). It thus appears probable that the product of m.p. 112° corresponds to structure IVb. Direct proof for this assumption is being sought by an independent synthesis. If formula IVb is accepted, it becomes evident that no counterpart of this product is observed in the Meerwein reaction of cinnamic acid, which according to Koelsch[5] can be represented by the following scheme.

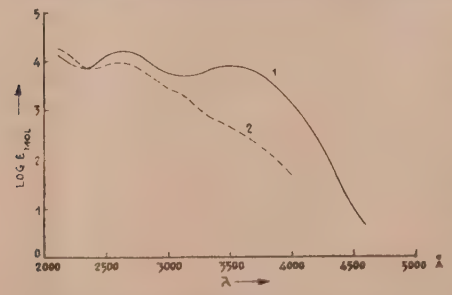


Figure 1— Absorption spectra in 95% ethanol.
1 — benzyl *p*-nitrophenyl ketone (IVb)
2 — phenyl *p*-nitrobenzyl ketone (IVa)

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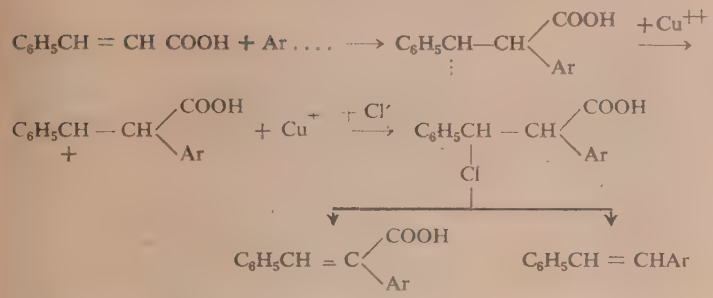
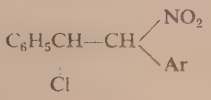
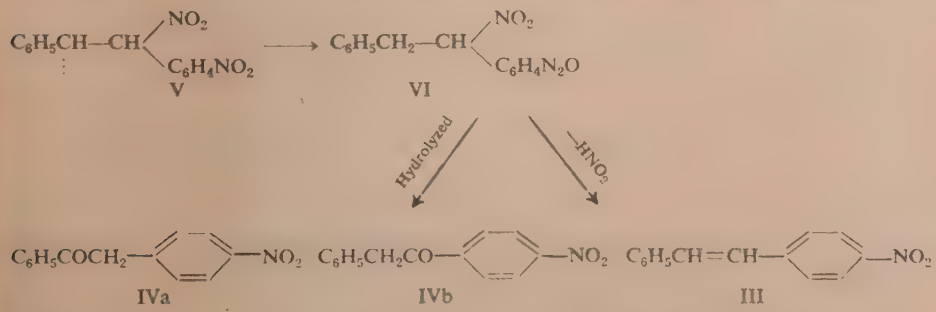


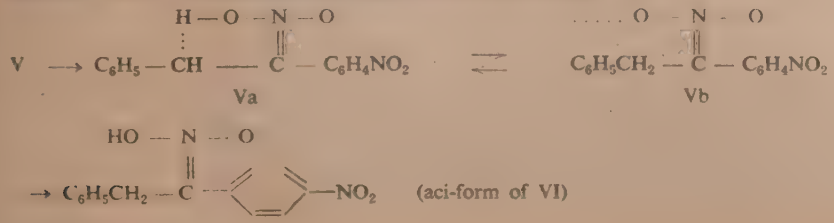
On this basis we should expect in the reaction with β-nitrostyrene the following intermediate:



which could eliminate either HNO_2 or HCl to yield a trisubstituted ethylene or else could eliminate both these molecules to give *p*-nitrotolane. The latter, however, can be expected to undergo hydration to the ketone IVa and not to IVb. Since neither of the actual products of the reaction corresponds to the predictions of this scheme, it must be concluded that a different mechanism applies in the case of β-nitrostyrene. Both products, III and IVb, can be derived from a single reaction path in the following way: The intermediate radical V becomes stabilized by picking up a hydrogen atom and forms the saturated nitroethane VI. This compound can split off HNO_2 to give *p*-nitrostilbene, but is also partly hydrolyzed to the ketone IVb, in analogy to the reaction observed by Nef[6,7] for nitroparaffins.



The curious behaviour of the radical V, which is in contrast to the intermediate radical in Koelsch's scheme, must be ascribed to the presence of the β-nitro group, which in its aci-form (as in Va) can tautomerize to the radical Vb. Thus instead of a carbon radical, now a nitro radical appears, which stabilises itself by the addition of hydrogen to give the aci-form of VI.



EXPERIMENTAL

To a solution of β-nitrostyrene (20 g) in acetone (400 ml), cooled to 0°, was added a clear solution of diazotized *p*-nitroaniline. Then a saturated solution of sodium acetate (41 g) and of cupric chloride (4.6 g) was added. Evolution of nitrogen started at +8°. After $1^1/_2$ hrs. the temperature was raised to 25° and kept constant for an additional period of $1^1/_2$ hrs. The mixture was then steam-distilled and the residue extracted with benzene, washed with acid and carbonate, and the solvent was removed. The red-brown residue (24 g) was triturated with ethanol, and the solid precipitate recrystallized first from this solvent, then several times from acetic acid. *p*-Nitrostilbene was obtained in yellow needles of m.p. 154—155°. It was identified by comparison of the stilbene and its dibromide with authentic samples[8].

The mother liquors were collected and distilled in vacuo at 230—240° (3 mm). Fractional crystallization gave 1.4 g of *p*-nitrostilbene (total yield: 2.5 g) and in addition 2.5 g of a yellow product, which crystallized from ligroine in yellow needles of m.p. 112—114°. (IVb).

Anal.: Found—C, 70.2; H, 4.6; N, 6.2%. Calcd. for $C_{14}H_{11}O_3N$—C, 69.7; H, 4.5; N, 5.8%.

The substance gave a red-brown colour, when heated with ethanolic KOH for a few minutes.It formed a red 2,4-dinitrophenylhydrazone of m.p. 239—240° (butyl acetate).

Anal.: Found—N, 16.6%. Calcd. for $C_{20}H_{15}O_6N_5$—N, 16.6%.

The isomeric ketone (IVa) was prepared by nitration of desoxybenzoin according to Petrenko[9]. Its 2,4-dinitrophenylhydrazone melted at 233—234° [10] and depressed the m.p. of the foregoing derivative.

REFERENCES

1. Hurd, Nilson and Wikholm, 1950, *J. Amer. Chem. Soc.*, **72**, 4697.
2. Meerwein, Buchner and van Emster, 1939, *J. prakt. Chemie*, **152**, 237.
3. Barnes, 1943, *J. org. Chem.*, **8**, 153.
4. Lifshitz, 1922, *Ber.*, **55**, 1633.
5. Koelsch and Boekelheide, 1944, *J. Amer. Chem. Soc.*, **66**, 412.
6. Nef, 1894, *Ann.*, **280**, 263.
7. Tamelen and Thiede, 1952, *J. Amer. Chem. Soc.*, **74**, 2615.
8. Pfeiffer and Sergiewskaja, 1911, *Ber.*, **44**, 1109.
9. Petrenko-Kritschenko, 1892, *Ber.*, **25**, 2242.
10. Womack, Campbell and Dodds, 1938, *J. Chem. Soc.* 1402.

DIETHYL OXALO-FLUOROACETATE

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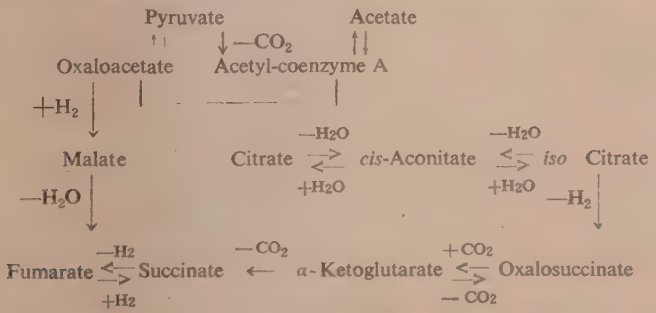
The curious fact that as simple a substance as fluoroacetic acid is one of the most powerful poisons known, has been ascribed by Bartlett and Barron[1] to a competitive blocking of acetate oxidation in the organism. The observation first made by Kalnitzky and Barron[2] that one of the characteristic effects of fluoroacetate poisoning is the accumulation of citric acid, has been extended by Martius[3] and by Liebecq and Peters[4], into the following theory:

Fluoroacetate is not toxic *per se*, but is transformed in the organism into a toxic compound of the type of fluorocitrate, which acts as an anti-metabolite and interferes with the utilisation of citrate and thus with the Krebs cycle. Indeed, Elliott and Kalnitzky[5], by incubating fluoroacetate with rabbit kidney cortex, were able to demonstrate the formation of a substance which gave positive tests for both fluorine and citric acid. Buffa, Peters and Wakelin[6] isolated this "inhibitor substance" and identified it as a fluorotricarboxylic acid, which specifically inhibits the enzyme aconitase[7].

In the light of this "jamming" theory of fluoroacetate poisoning, it appeared interesting to prepare and study the physiological behaviour of the intermediate compounds of the Krebs cycle, replacing in each step one hydrogen by a fluorine atom.



The present study is devoted to the synthesis of diethyl oxalo-fluoroacetate which from a chemical point of view is also the ideal starting material for the preparation of fluoropyruvic acid. An attempt to replace the chlorine atom in Wislicenus' diethyl oxalo-chloroacetate[8] by fluorine failed: both without solvent and in acetamide[9], the temperature required for the reaction to take place was so high that decomposition occurred. It was possible, however, to condense diethyl oxalate with ethyl fluoroacetate. When the condensation was carried out in presence of alcohol-free sodium ethoxide, 65—80% yields of the sodium enolate of diethyl oxalo-fluoroacetate were obtained, as has been briefly reported elsewhere[10]. The free ester could be characterised by its infrared spectrum*. This showed a broad, very strong band from 1738 to 1750 cm^{-1}, representing the combined absorption of the keto and the ester groups, a band at 1094 cm^{-1} (optical density $d = 1.1$) which is assigned to the C—F bond, and two bands at 1440 cm^{-1} ($d = 0.040$) and 1368 cm^{-1} ($d = 0.60$), respectively, which belong to the methyl radicals in the ethyl groups.

The C—F absorption is located at 1045 cm^{-1} in fluoroacetic acid; it was to be expected that the neighbourhood of the carbonyl double bond would raise the wave number of the C—F band. For analogous reasons, also the carbonyl frequency in diethyl oxalo-fluoroacetate is unusually high; a similar effect of *bromine* atoms has been observed by Jones et al.[11].

* The infrared analysis was kindly performed by Dr. S. Pinchas of the Weizmann Institute of Science, Rehovot.

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An attempt to prepare free oxalo-fluoroacetic acid by saponification of its ester with cold concentrated hydrochloric acid gave a crystalline solid, identified as oxalic acid, and, in the filtrate, a ketonic substance which afforded a voluminous 2.4-dinitrophenylhydrazone. Evidently "acid fission" and "ketonic fission" have taken place simultaneously under these conditions, under which the parent substance, diethyl oxaloacetate, gives mainly pyruvic acid and a small percentage (5%) of oxaloacetic acid, but no oxalic acid. Also when the ester was heated with dilute hydrochloric acid, there was formed oxalic acid and a ketonic compound which gave readily a dinitrophenylhydrazone and a semicarbazone (the ketonic compound is apparently fluoropyruvic acid; see below). Using a method which has proved effective in similar cases[12,13], we tried to obtain the free oxalo-fluoroacetic acid by catalysed pyrolysis of its *tert.*-butyl ester. The latter was prepared by Claisen condensation between *tert.*-butyl oxalate and *tert.*-butyl fluoroacetate, best yields being obtained with alcohol-free potassium *tert.*-butoxide as condensing agent. No self-condensation of *tert.*-butyl fluoroacetate took place under these conditions. Pyrolysis of the ester was carried out by refluxing its benzene solution in the presence of a trace of *p*-toluenesulphonic acid. On cooling, a crystalline precipitate was obtained that contained the free acid, as it gave a very intense and quickly fading colour reaction with ferric chloride and afforded a well defined dinitrophenylhydrazone. When the aqueous solution of the product was heated for several minutes at 100°, the ferric chloride reaction became negative, but dinitrophenylhydrazine still produced a precipitate. This behaviour is best explained as due to the ready loss of carbon dioxide and formation of fluoropyruvic acid. However, it has not been possible so far to prepare a pure sample of oxalo-fluoroacetic acid, because of its pronounced tendency to spontaneous decarboxylation, and also because even under these mild conditions 'acid fission' leading to formation of oxalic acid could not be avoided. It should be pointed out, that under the same conditions pyrolysis of *tert.*-butyl oxaloacetate does not give even traces of oxalic acid.

Fluorine substitution in oxaloacetic acid has a decisive influence on the behaviour of this substance. This is already expressed in the transient nature of the colour reaction with ferric chloride, but a more fundamental difference has been revealed through a comparison of the enol-keto-equilibria of the parent substance and the fluoro-derivative. Using the indirect method of K.H. Meyer[14], the following values (in % enol) were obtained for the fluorine compound*. Homogeneous ester, 0.8—0.9%; 0.1 M solution in anhydrous alcohol, 0.35—0.45 %; 0.1 M solution in hexane, 0.6%, whilst for the pure parent substance a value of 72—80% has been reported[15].

The toxicity of the sodium enolate of diethyl oxalo-fluoroacetate has been determined for rats and mice. The substance proved to be relatively non-toxic, LD_{50} being for mice 750 mg/kg. On the other hand, it is a much more powerful inhibitor of bacteria than fluoroacetate. The growth of *Aerobacter aerogenes*, e. g., is inhibited to the same degree by concentrations 50 times smaller than those of fluoroacetate[16]. This surprising behaviour may be due to different metabolism of the oxalo-fluoroacetate in animals and bacteria; however, it is also possible that the non-toxicity of the compound for animals is due to its inability to cross the mitochondrial barrier within which the enzymes of the Krebs cycle are located[17], whilst in bacteria the substance is able to reach easily the site of action.

A decision on this point must be left to further experimentation. At present it can only be stated that the strong inhibition produced by oxalo-fluoroacetate tends to sustain the opinion expressed by several authors[18] that the tricarboxylic acid cycle in its complete or abridged form exists also in bacteria.

EXPERIMENTAL

Diethyl oxalo-fluoroacetate. To a suspension of alcohol-free sodium ethoxide, prepared from 23 g of metallic sodium in 200 ml of anhydrous ether, 146 g of freshly distilled diethyl oxalate and, after a few minutes, 106 g of ethyl fluoroacetate were added dropwise. After adding one third of the ethyl fluoroacetate, a yellow precipitate suddenly appeared which increased in the course of further addition. The mixture was allowed to stand for 24 hours at room temperature; then the solid sodium enolate of diethyl oxalo-fluoroacetate was washed several times with ether until the filtrate was colourless and dried. Weight, 180 g. The *enolate* is a cream-white, hygroscopic powder which turns yellow on standing. It is soluble in water and alcohol, insoluble in ether and hydrocarbons, and gives the characteristic colour reaction of β-keto-acid derivatives with alcoholic ferric chloride solution.

A solution of 100 g of the enolate in 50 ml of cold distilled water was acidified in a separatory funnel with dilute sulphuric acid to *p*H1—2 and extracted repeatedly with ether. The ethereal extract was dried over sodium sulphate and the solvent

* The keto-enol-equilibria measurements were made by Mrs. Ch. Klebansky

evaporated. The free *diethyl oxalo-fluoroacetate* (60 g) distilled at 120 – 122° 9 mm. as a colourless oily liquid, soluble in alcohol and ether, insoluble in water and hydrocarbons. With an alcoholic solution of ferric chloride, it gives a deep-brown colour reaction, which fades quickly on standing. d_4^{20}, 1.261 ; n_D^{20}, 1.42; MR calcd., 42.16; MR found, 42.38.

The 2,4-*dinitrophenylhydrazone* of the ester was recrystallised from alcohol and melted at 124° *Anal* Calcd. for $C_{14}H_{15}N_4O_8F$: C, 43.7; H, 3.9; N, 14.6. Found: C, 44.2; H, 4.0; N, 13.9.

tert.-Butyl fluoroacetate was prepared by a method similar to that used by Westheimer and Shockhoff[19] for the preparation of *tert.*-butyl chloroacetate. B.p. 129.5 – 131°; d_4^{20} 0.9904; n_4^{20} 1.386; MR calcd., 31.42; MR, found, 31.82. *Anal.* Calcd. for $C_6H_{11}O_2F$: C, 53.8; H, 8.2. Found: C, 54.2; H, 8.2.

tert.-Butyl oxalo-fluoroacetate. Alcohol-free potassium *tert.*-butoxide, prepared from 2.4 g of metallic potassium and 75 ml of anhydrous *tert.* butanol, was suspended in 50 ml of ether and 12.8 g of di-*tert.* butyl oxalate, prepared according to Backer and Homan[20], and 8 g of *tert.*-butyl fluoroacetate added successively with shaking. After several minutes, a voluminous precipitate was formed. The mixture was allowed to remain overnight at room temperature, and the *potassium enolate of di-tert. butyl-oxalo-fluoroacetate* isolated as a white, very hygroscopic powder, soluble in water and alcohol, insoluble in hydrocarbons.

The *free ester* was prepared from the enolate in a way similar to that described above for the diethyl compound. It solidifies at about 15°, and is soluble in benzene, chloroform and ethyl acetate, insoluble in non-polar solvents. With alcoholic ferric chloride solution, it gives a very faint colour reaction.

The 2,4-*dinitrophenylhydrazone*, recrystallised from alcohol, formed fine needles, m.p. 137-8°. *Anal.* Calcd. for $C_{18}H_{23}N_4O_8F$: C,48.7; H,5.6; N,12.7. Found: C,48.5; H,5.4; N,12.1.

The carbon-hydrogen determinations were carried out according to the method of Bodenheimer and Goldstein[21].

REFERENCES

1. Bartlett and Barron, 1947, *J. biol. Chem.*, **70**, 67.
2. Kalnitzky and Barron, 1948, *Arch. Biochem.*, **19**, 75.
3. Martius, 1949, *Ann.*, **561**, 227.
4. Lifbecq and Peters, 1949, *Biochem. Biophys. Acta*, 3, 215.
5. Elliott and Kalnitzky, 1950, *J. biol. Chem.*, 186.
6. Buffa, Peters and Wakelin, 1951, *Biochem. J.*, **48**, 467.
7. Peters, 1952, *Proc. Roy. Soc.*, **B139**, 143.
8. Wislicenus, 1910, *Ber.*, **43**, 3529.
9. Blank and Bergmann, 1952, *Bull. Res. Counc. of Israel*, **2**, 71.
10. Blank, Bergmann and Mager, 1953, *Bull. Res. Counc. of Israel*, **2**, 287
11. Jones *et al.*, 1952, *J. Amer. Chem. Soc.*, **74**, 2828.
12. Breslow, Baumgarten and Hauser, 1944, *J. Amer. Chem. Soc.*, **66**, 1286.
13. Heidelberger and Hurlbert, 1950, *J. Amer. Chem. Soc.*, **72**, 4704.
14. Meyer, K. H., 1930, *Annual Rep. Progress Chem.*, **27**, 106.
15. Meyer, K. H., 1912, *Ber.*, **45**, 2860. This value has been confirmed in this laboratory by Mrs. H. Klebansky.
16. Mager *et al.*, unpublished results.
17. Lehninger, 1945, *J. Biol. Chem.*, **157**, 363.
18. Ael, 1951, *Bacteriol. Rev.*, **15**, 211.
19. Westheimer and Shockhoff, 1940, *J. Amer. Chem. Soc.*, **62**, 271.
20. Backer and Homan, 1939, *Rec. Trav. Chim. Pays-Bas*, **58**, 1048.
21. Bodenheimer and Goldstein, 1953, *Bull. Res. Counc. of Israel*, 3 53.

CARBON-BENZYLATION BY MEANS OF BENZYL ALCOHOL

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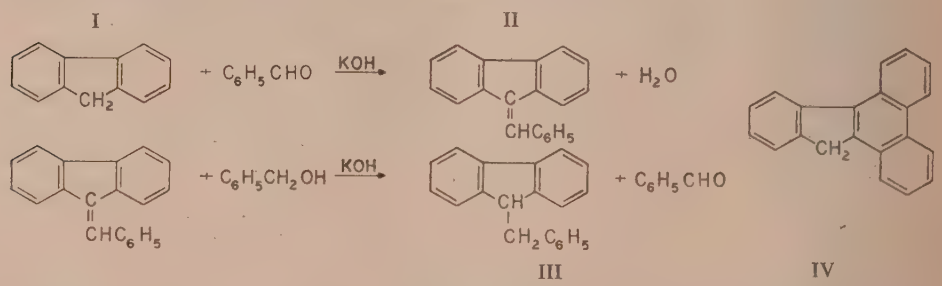
The various methods available in the literature for the preparaton of 9-benzylfluorene (III) employ derivatives, obtained from fluorene (I) by substitution in the 9-position. Such are, for example, 9-formylfluorene[1] and 9-carbethoxylfluorene[2], which may be alkylated by benzyl chloride, with subsequent elimination of the formyl and carboxyl groups, respectively. Likewise, 9-benzylfluorene has been obtained by reduction of benzylidenefluorene (II), either with aluminium amalgam[3] or catalytically, in presence of a palladium catalyst[4]. A more direct method of benzylation could, perhaps, be seen in the interaction of benzyl chloride and 9-fluorenyllithium, obtained from fluorene and phenyllithium[5].

It has now been found that 9-benzylfluorene may be prepared conveniently and in quantitative yield by heating fluorene and benzyl alcohol in presence of a small amount of potassium hydroxide and traces of benzaldehyde. Although the reaction may be carried to completion by refluxing the mixture, removal of the water accelerates it considerably, presumably owing to a higher temperature achieved.

In a typical experiment, a mixture of fluorene of melting point 114.8—5.6° (4.15 g), benzyl alcohol (7 ml), potassium hydroxde (0.1 g) and benzaldehyde (0.05 ml) was kept at boiling temperature for 15 minutes, and the water formed allowed to distil off. After cooling, the reaction mixture was treated with water (7 ml), and the crystalline product was filtered and washed with water. There was obtained 6.35 g of 9-benzylfluorene, m. p. 133 — 4.4°. After recrystallisation from heptane it melted at 134—5°. (Literature 134—5°).

The conversion of fluorene to 9-benzylfluorene is considered to be the result of two consecutive reactions: In the first, fluorene condenses with benzaldehyde to yield benzylidenefluorene; in the second, the latter is reduced by benzyl alcohol (or potassium benzylate) to 9-benzylfluorene, the benzaldehyde reformed in the reduction thus becoming available for further reaction:



This assumption is borne out by the following observations:

(1) Benzylidenefluorene is rapidly and quantitatively reduced to the 9-benzyl compound when heated with benzyl alcohol and potassuim hydroxide in excess of the amount necessary for the Canizzaro reaction of the benzaldehyde formed in the reduction. In accordance with the theory, one half mole of potassium benzoate is produced per mole of benzylidenefluorene used.

(2) Fluorene readily condenses with benzaldehyde in benzyl alcohol solution containing potassium hydroxide, to form benzylidenefluorene in excellent yield, when the reaction is carried out at a temperature (110°) low enough to prevent reduction of the product formed.

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(3) Fluorene was recovered unchanged when treated with benzaldehyde-free benzyl alcohol and potassium hydroxide in an atmosphere of nitrogen under conditions otherwise identical with those described above*.

Substituted fluorenes, such as 2-methyl-, 2-bromo-, 2,7-dibromo-, 1,2,3,4-dibenzo- (IV) and 2-hydroxy-fluorene, are benzylated in the 9-position with equal ease. In the case of the last mentioned compound, potassium hydroxide was used in excess of the amount required for the neutralisation of the phenolic hydroxyl group.

The remarkable reducing properties of hot benzyl-alcoholic solutions of potassium (and sodium) hydroxyde have been demonstrated by Palfray, Sabetay and their collaborators[8,9,10] for carbonyl compounds and allyl alcohols. They appear to be associated with the polar character of the double bond to be reduced, whether inherent (carbonyl group) or induced (ethylenic bond of the allyl alcohol system). The easy response of benzylidenefluorene, which recalls its easy reduction by aluminium amalgam[3], would then be in line with the observations by Bergmann and Lavie[11], made in the course of extensive investigations on the properties of fulvenes carried out by Bergmann, Pullman and their collaborators in recent years[12], that the semicyclic double bond in this group of compounds could be reduced with lithium aluminium hydride, presumably on account of thr polar character of this bond. It should be recalled in this connection that, in confirmation of predictions made by Pullman, Coulson and others on theoretical grounds[13], it has been shown[13] that fulvenes, including benzylidenefluorene, possess a finite dipole moment.

The study of the reducing and benzylating action of benzyl alcohol under alkaline conditions on other types of organic compounds is being pursued in this laboratory.

* On prolonged heating, 9-benzylfluorene gradually appeared in the reaction mixture. This is hardly surprising, as in presence of alkali, benzyl alcohol might be expected[7] to undergo slow dehydrogenation at the temperature used; indeed, the smell of benzaldehyde was perceptilble under these conditions.

REFERENCES

1. Brown and Bluestein, 1943, *J. Amer. Chem. Soc.*, **65**, 1082.
2. Wislicenus and Mocker, 1913. *Ber.*, **46**, 2772.
3. Thiele and Henle, 1906, *Annalen*, **347**, 290.
4. Bergmann, 1930, *Ber.*, **63**, 1617.
5. Wittig, Davis and Koenig, 1951, *Ber.*, **84**, 627.
6. Thiele, 1900, *Ber.*, **33**, 851.
7. See e.g. Guerbet, 1908, *Bull. Soc. chim. France*, 500.
8. Palfray and Sabetay, 1935, *Compt. Rend.*, **200**, 404.
9. Mastagli, 1938, *Ann. Chim.*, **10**, 281.
10. Mastagli, Charreire and Lambert, 1945, *Compt. Rend.*, **221**, 749.
11. Lavie, 1951, *This Journal*, **1**, No. 1—2, 135: Lavie and Bergmann, 1951, *Bull. Soc. chim. France*, 250.
12. Bergmann, Pullman and Collaborators, 1950 1951, 1952, *Bull. Soc. chim., France.*
13. For references see Bergmann and Fischer, 1950, *Bull. Soc. chim. France*, 1084.

SOME ASPECTS OF CARCINOGENESIS

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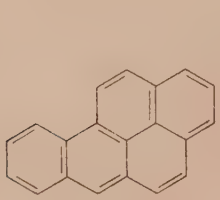
Among the many phases of Dr. Weizmann's contributions to science, his pioneering studies on synthetic reactions in the fields of aromatic hydrocarbon chemistry paved the way for the subsequent advances in chemical carcinogenesis. It is fitting, therefore, that a memorial volume dedicated to his memory should include a communication on carcinogenesis. In fulfilling this task, I am privileged to pay homage to a great man and inspiring scientist.

Experimental carcinogenesis owes its inception to three basic discoveries:— (1) the early clinical observation by Pott, in 1775, that certain skin cancers among chimney-sweeps are occupational in origin; (2) the experimental demonstration by Yamagiwa and Itchikawa, in 1914, that tumours could be induced artificially in animals by repeatedly painting their skin with coal-tar; and (3) the isolation and identification by Cook, Hewett and Hieger, in 1933, of 3:4-benzpyrene (I) as a potent carcinogenic constituent of tar. The subsequent synthesis and biological testing of hundreds of compounds, both related to, and differing from, the polycyclic hydrocarbons, brought to light a wide range of carcinogens[1], and provided the necessary tools for the detailed study of carcinogenic action.

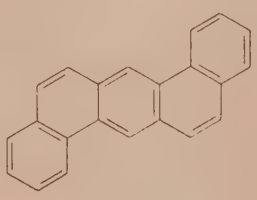
Apart from the systematic accumulation of carcinogenic data[1-5], progress has also been made, during the past twenty years, on the mechanism of carcinogenic action[2-9]. The latter may conveniently be considered under three headings:— (1) from the viewpoint of the carcinogen (for a possible correlation between structure and function), (2) from the metabolic angle (to determine what role the metabolites of carcinogens play in the carcinogenic action), and (3) from the biological angle (concerning the nature of the changes in the tissues during the neoplastic transformation).

1. THE MECHANISM OF ACTION FROM THE VIEWPOINT OF THE CARCINOGEN

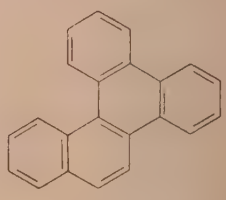
Of the fifteen possible 5-ring polycyclic aromatic hydrocarbons, only 3:4-benzpyrene (I), 1:2:5:6-dibenzanthracene (II) and 1:2:3:4-dibenzphenanthrene (III) are definitely carcinogenic, the remaining twelve being inactive, or displaying at most only traces of activity[1].



(I)
3:4-benzpyrene



(II)
1:2:5:6-dibenzanthracene



(III)
1:2:3:4-dibenzphenanthrene

Compounds (I) and (II) may be considered derivatives of 1:2-benzanthracene (IV); compound (III), a derivative of 3:4-benzphenanthrene (V); while (I) and (III), may also be considered derivatives of chrysene (VI). Of these three key compounds, 3:4-benzphenanthrene is mildly carcinogenic, 1:2-benzanthracene has borderline activity, while chrysene is non-carcinogenic. Many alkyl derivatives of these compounds are, however, more active than the parent hydrocarbons, *depending on the positions of substitution*. Thus, of the twelve possible methyl-1:2-benzanthracenes, the 9- and 10-derivatives are highly active; the 3-, 4-, 5- and 6- are moderately active, the 7- and 8- are weakly active, while

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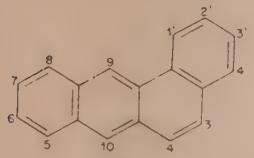
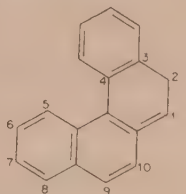
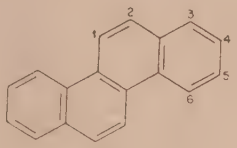
the 1′-, 2′-*,3′- and 4′- are non-carcinogenic. With 3:4-benzphenanthrene, greatest activity occurs when substitution is in the 2- position, and with chrysene, in the 1- position. Di- and trimethyl substitution confers greater carcinogenic activity to 1:2-benzanthracene than mono-substitution, provided these



(IV)
1:2-benzanthracene



(V)
3:4-benzphenanthrene

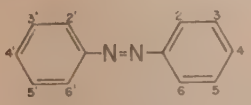


(VI)
chrysene

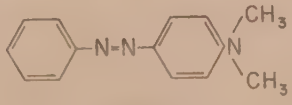
occupy the 'active' positions. Ethyl and propyl groups are also effective, but activity rapidly falls off with further lengthening of the side chain. Polar groups and halogen substitutents are, on the whole, unfavourable for carcinogenesis, while other substituents have an unpredictable effect. Hydrogenation of any part of the ring system usually leads to loss of activity; a thiophene or pyridine nucleus in the place of one of the benzene rings does not interfere with carcinogenic activity (though this depends on the ring involved); while an oxygen-containing ring renders the compound inactive. Some activity has even been obtained with substituted 3-ring hydrocarbons, e.g. with 1:2:3:4-tetramethylphenanthrene and with 9:10-dimethylanthracene.

Thus, while the configuration of the hydrocarbon molecule does influence carcinogenic activity, the early hopes of finding a close correlation between structure and function has not been realized.

This became all the more apparent with the discovery of 'remotely-acting' carcinogens, with tumour production restricted to certain specific organs. The most interesting series, for the present discussion, are the dimethyl-amino-derivatives of azobenzene (VII), which, when fed continuously, produce tumours of the liver. Of these, the two best known examples are 2′:3-dimethyl-4aminoazobenzene (*o*-aminoazotoluene) and 4-dimethylaminoazobenzene (VIII). Subsequent studies demonstrated once again the importance of the position of substitution for carcinogenic activity[10]. Among the isomers



(VII)
azobenzene



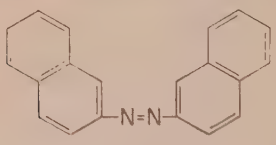
(VIII)
4-dimethylaminoazobenzene

of 2′:3-dimethyl-4-aminoazobenzene, pronounced activity was found with 2′:5-dimethyl-2-aminoazobenzene and with 2:4′-dimethyl-4-aminoazobenzene, but little or no effect with other configurations. A study of derivatives of 4-dimethylaminoazobenzene (VIII) also provided some interesting results, high activity being obtained with an additional methyl group in the 3′- position, but complete loss of activity when in the 2- or 3- position. Fluoro-derivatives were active in many positions of substitution; choro- and nitro- derivatives, less so; while hydroxy-derivatives were, without exception, inactive for liver carcinogenesis. (yet 4-hydroxyazobenzene is carcinogenic for the stomach epithelium, and 4-hydroxy-2′:3-dimethylazobenzene is carcinogenic for the urinary bladder.) When the -N=N- linkage in (VIII) is replaced by -N=CH- or -CH=N-, activity is lost; yet when replaced by a -CH=CH- linkage (i.e. 4-dimethylaminostilbene), there is marked carcinogenic activity.

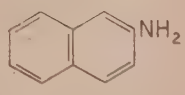
The fact that 2:2′-azonaphthalene (IX) is also carcinogenic for the liver, is of particular interest, in view of its structual relationship to 2-naphthylamine (X), which is carcinogenic for the urinary bladder, and to 3:4:5:6- dibenzcarbazole (XI), which is a potent 'locally-acting' carcinogen (*i.e.* with carcinogenic properties similar to those of the aromatic polycyclic hydrocarbons).

* In some unpublished experiments by the author, slight activity was, however, observed with 2′-methyl-1:2-benzanthracene.

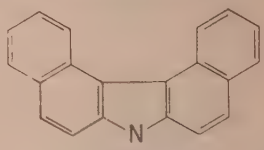
When it became evident that carcinogenesis could not be attributed to one particular chemical configuration, consideration was given to physicochemical properties as a possible determinant of carcinogenic action, with emphasis on the electron densities at specific regions in the molecule — *e.g.* at the



(IX)
2:2'-azonaphtalene



(X)
2-naphtaylamine



(XI)
3:4:5:6-dibencarbazole

angular (phenanthrenoid) double bond (or K region), in the case of polycyclic aromatic hydrocarbons, and at the azo linkage (or K′ region), in the case of the azo dye carcinogens[11]. But, the validity of quantitatively correlating calculated values for electron densities with observed values for carcinogenic potencies, is questionable[12], on the following grounds: —

(1) The carcinogenic potency of a compound is a variable value, depending on the particular tissue, strain, and species of animal used as test object. The most potent carcinogen, under one set of conditions, may be entirely non-carcinogenic, under another. In fact, the data in the literature are restricted to very limited conditions, and cannot, therefore, serve as representative values in any quantitative sense.

(2) Such a correlation fails to take into account the possibility that some carcinogens may owe their acton to products of their metabolism, in which case, the properties of the metabolites, rather than of the original compounds, have relevance in this connection.

(3) From the biological angle, carcinogenesis is also not a single process, but comprises independent stages, for which a single composite value is deceptive.

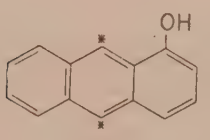
(4) There are, in addition, many other chemical carcinogens (e.g. urethane, carbon tetrachloride, arsenic, beryllium compounds, etc.) as well as physical carcinogens (heat, cold, radiations, etc.) for which a correlation with electron densities at a 'K region' is clearly inapplicable.

In short, there can be no single over-all correlation between the physical or chemical structure of a compound and its carcinogenic activity, if the latter is itself not a single process, but consists of a chain reaction. The evidence for such a chain reaction, both in the biochemical and biological sense, must be taken into account in attempting to determine the mechanism of carcinogenic action.

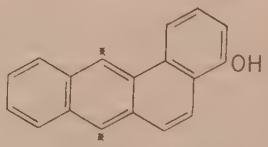
2. THE MECHANISM OF ACTION FROM THE METABOLIC ANGLE

Chemical carcinogens undergo oxidative and other metabolic changes in the body, and several of the products have already been identified and, in a few cases, tested for carcinogenic activity[5,13]. The results are of special interest biochemically, illustrating certain unexpected metabolic pathways, and also biologically, indicating possible mechanisms of carcinogenic action.

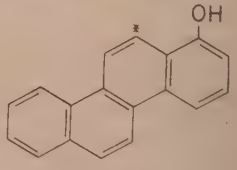
When polycyclic aromatic hydrocarbons are administered to animals, phenolic derivatives are excreted, which differ from those obtained when the compounds are treated *in vitro* with strong oxidizing agents. The metabolites (XII, XIII, XIV, XV, XVI, XVII) display points of attack which do not cor-



(XII)
1-anthranol

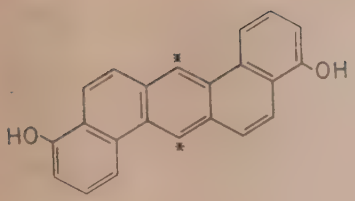


(XIII)
4'-hydroxy-1:2-benzanthracene

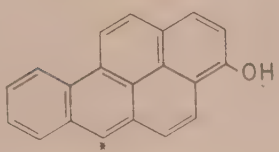


(XIV)
3-chrysenol

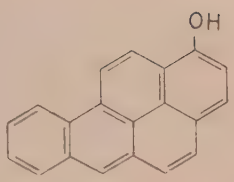
respond to the reactive positions (marked with an asterisk in the above formulae), where oxidation *in vitro* normally occurs. A partial explanation of this may be that while ordinary oxidation is substitutive in type, metabolic oxidation (certainly in the case of anthracene, and presumed also in the other cases)



(XV)
4':8'-dihydroxy-1:2:5:6-dibenzanthracene

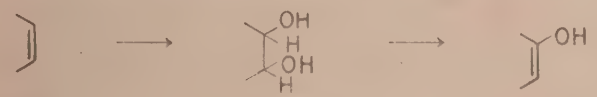


(XVI)
8-hydroxy-3:4-benzpyrene



(XVII)
10-hydroxy-3:4-benzpyrene

is additive, or by perhydroxylation — *i.e.* with the formation of an intermediary dihydroxy-dihydro-derivative, which, with the loss of a molecule of water, is converted into a phenol (XVIII, XIX, XX). This does not explain, however, why the positions of attack are as found, namely, in the *α* positions



(XVIII) (XIX) (XX)

to the phenanthrenoid double bonds, *instead of actually at these double bonds*, as happens when perhydroxylation is obtained synthetically by treatment with hydrogen peroxide and osmium tetroxide. Metabolic studies with C^{14}-labelled hydrocarbons indicate that these compounds undergo further changes in the body, involving actual cleavage of the ring structure[14].

Only a few of the metabolites have so far been tested for carcinogenic activity, and the implications of the results must, therefore, be interpreted with caution. Of the phenolic metabolites, 4′-hydroxy-1:2-benzanthracene and 4′:8′-dihydroxy-1:2:5:6-dibenzanthracene are non-carcinogenic, while 8-hydroxy-3:4-benzpyrene has only slight activity. On the other hand, the methylated product of 8-hydroxy-3:4-benzpyrene proved to be one of the most powerful carcinogens known[15]. If the animal body is capable of methylating, or otherwise protecting, the hydroxyl group, the oxidative metabolic process may, after all, be implicated in carcinogenesis, despite the fact that the phenols themselves appear biologically inactive.

It is interesting to note, in this connection, that while the carcinogenic action of 2-naphthylamine on the urinary bladder only operates when the substance is administered remotely (*i.e.* by feeding or by subcutaneous injection), its metabolite — 1-hydroxy-2-naphthylamine — is locally carcinogenic (i.e. when introduced into the bladder itself).[16]

The metabolism of azo dye carcinogens has also been investigated in some detail. Of the metabolic products so far isolated — involving demethylation and cleavage at the azo linkage — only the monomethyl derivative was found to possess any carcinogenic activity[10].

Much more data are needed to establish the role of metabolism in the carcinogenic process; but the available evidence is at least suggestive that, in certain cases, metabolites of carcinogens are involved in the biological mechanism.

3. THE MECHANISM OF ACTION FROM THE BIOLOGICAL VIEWPOINT

The biological approach to the problem differs radically from those so far discussed, in that the emphasis is on the responding tissue instead of on the inciting agent. Whatever the nature of the carcinogen or its metabolic fate in the body, the actual process of transformation of normal cell into a tumour cell is essentially biological in nature, operating within the framework of the functional potentialities of the living cell.

A unique feature of the neoplastic response of living tissue to carcinogenic action is the long latent period from the commencement of treatment to the first appearance of the tumour. The proliferative changes during the latent period are not readily distinguishable from non-neoplastic proliferation; yet, associated with this apparently unspecific phase, the essential changes concerned with the specific

neoplastic transformation must be taking place. Since these are not morphologically distinguishable, experimental methods had to be devised to demonstrate their presence and nature.[17,6,7,9]

It has previously been established[17] that while irritation *per se* is not carcinogenic, it can modify the neoplastic response to a carcinogenic agent, inhibiting the process in some cases ('anticarcinogenic action') and augmenting it in others ('cocarcinogenic action'). The latter was particularly well exemplified by the non-carcinogenic agent, croton oil, which, when added to a dilute solution of a carcinogen and appied to mouse's skin, raised the tumour incidence to a remarkable degree. In subsequent experiments, in which the carcinogen and the croton oil were applied during separate periods, augmentation of carcinogenesis occurred when the croton oil treatment was begun after cessation of the carcinogenic treatment, but not when it preceded it.

The fact that croton oil could complete the carcinogenic process but could not initiate it, pointed to the existence of distinctive stages of carcinogenesis with independent mechanisms. A similar conclusion was reached from other investigations, *e.g.* from a study of the factors influencing the disappearance and reappearance of induced skin tumours in rabbits.[18]

It was shown that initiating action represented a sudden conversion of normal cells into 'latent' or 'dormant' tumour cells, which could remain quiescent indefinitely unless stimulated by subsequent 'promoting action' to assume the properties of a growing tumour. The precise nature of these two stages is, however, still not clearly understood. The rapidity of development of the initiating process, and its irreversible character, suggests a mutation-like action, though the evidence in favour of it being due to an actual somatic mutation is still inconclusive. The slowness of development of the promoting process, and its apparent dependence on speeding up the growth of the 'dormant tumour cells', suggested, at first, that the action was essentially a non-specific cell-proliferating influence. This is, however, definitely not the case, since many agents which can induce hyperplasia as effectively as croton oil, fail to act as promoting agents.

The carcinogens used experimentally in animals, and those responsible for environmental cancer in man, possess both initiating and promoting action. The problem would obviously assume great complexity if in certain conditions (*e.g.* in the development of spontaneous tumours of intrinsic origin), separate factors would be responsible for these two stages of carcinogenesis, and if, as seems not altogether outside the bounds of possibility, the promoting phase was brought about by a physiological disturbance in the normal functioning of the body, rather than by the action of some particular 'promoting agent'.

These speculative ideas are mentioned here in order to indicate some of the future lines of research along which the work is likely to develop.

Apart from the two stages of carcinogenesis already discussed, a further stage in the evolution of a tumour is becoming recognized, concerned with the development of 'biological autonomy' of a tumour[19,20] The transition in question does not exactly correspond to the older distinction between 'benign' and 'malignant' tumours. It is characterized by (i) an acquired independence from many of the controlling influences of the body; (ii) a strong tendency for metastasis formation, associated with a poor survival rate following radical operation; and (iii) an ability of the tumour to grow in the anterior chamber of the eye in a heterologous species.

This development of biological autonomy occurs spontaneously at some stage during the growth of the tumour (sometimes only after a number of serial transplantations). It cannot, as yet, be brought about artificially.

4. GENERAL CONCLUSIONS

The investigations of the past twenty years on the mechanism of carcinogenesis have brought to light much valuable information and have opened up promising fields of enquiry. Many of the fundamental problems involved are, however, still unsolved.

The precise structure of a carcinogen strongly influences its potency of action; yet the sought-for correlation between structure and function seems to be largely illusory. Some of the metabolites of carcinogens appear to be involved in the carcinogenic action; yet the extent to which they are implicated is not yet known. The neoplastic transformation of normal cells into tumour growths is made up of separate stages with independent mechanisms; yet the nature of these component phases is still a mystery.

That carcinogenesis is so complicated a process, is hardly surprising, in view of the diversity of manifestations of tumour growth, and the range of tissues, throughout the animal kingdom, that are capable of undergoing this specific transformation.

While some of the problems that await solution are already indicated above, there are other aspects of the problem, not touched upon in this review (e.g. concerning the role of tumour viruses), which will eventually have to be integrated, if the formulation of an all-embracing theory of the mechanism of carcinogenesis is to have any validity. In this, as in most other branches of science, the main danger is that of over-simplification, where truth is sacrificed on the altar of 'clarity'.

REFERENCES

(Most of the references given below are reviews. A few original papers are included which have appeared too recently to have been dealt with adequately in current reviews).

1. HARTWELL, J. L., 1951, "Survey of Compounds Which Have Been Tested for Carcinogenic Activity." 2nd Ed., U.S. Public Health Service, *Publ.* **149**, Fed. Security Agency, Washington, D.C.
2. FIESER, L. F., 1938, *Am. J. Cancer*, **34**, 37.
3. COOK, J. W. and KENNAWAY, E. L., 1938, *Am. J. Cancer*, **33**, 50; **39**, 381-428 & 521-582.
4. BADGER, G. M., 1948, *Brit. J. Cancer*, **2**, 309.
5. VARIOUS AUTHORS, 1947, *Brit. Med. Bull.*, **4**, Nos. 5 & 6.
6. VARIOUS AUTHORS, 1949, "Semaine d'Etude sur le Probleme Biologique du Cancer", *Pontif. Acad. Scient. Scripta Varia*, Vatican City.
7. BERENBLUM, I., 1952, "Clinical Problems in Cancer Research". Sloan-Kettering Inst. Seminar 1948-49, 125-143.
8. BOYLAND, E., 1952, *Cancer Res.*, **12**, 77.
9. BERENBLUM, I., 1953, *Advances in Cancer Research*, Academic Press Inc. **2**, (in press).
10. BADGER, G. M. and LEWIS, G. E., 1952, *Brit. J. Cancer* **6**, 270.
11. COULSON, C. A., 1953, *Advances in Cancer Research*, Academic Press Inc.,**1**, 1.
12. BERENBLUM, I., 1951, "Symposium on Chemical-Biological Correlation". *Nat. Res. Council, Publ.* **206**, Washington, 363.
13. VARIOUS AUTHORS, 1950, "Biological Oxidation of Aromatic Rings". *Biochem. Soc. Symposia No. 5*, Cambridge Univ. Press.
14. HEIDELBERGER, C. and WEISS, C. M., 1951, *Cancer Res.*, **11**, 885.
15. COOK, J. W. and SCHOENTAL, R., 1952, *Brit. J. Cancer*, **6**, 400.
16. BONSER, G. M., CLAYSON, D. B., JULL, J. W. and PYRAH, L. N., 1952, *Brit. J. Cancer*, **6**, 412.
17. BERENBLUM, I., 1944, *Arch. Path.*, **38**, 233.
18. FRIEDEWALD, W. F. and ROUS, P., 1944, *J. Exp. Med.* **80**, 101.
19. FOULDS, L., 1951, *Ann. Roy. Coll. Surg.*, **9**, 93.
20. GREENE, H. S. N., 1951, *Cancer Res.*, **11**, 899.

THE INFLUENCE OF POST-STIMULATION TIME-INTERVAL UPON THE EFFECTIVE INHIBITION BY BENADRYL OF DECIDUOMA FORMATION

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INTRODUCTION

The decidual cell reaction of the non-pregnant endometrium (or deciduoma), which is elicited in response to injury of the uterine mucosa, was first described by Loeb[1]. This phenomenon has been verified and extended to the rabbit[2] rat[3,4,5] dog[6] mouse[7] and monkey[8]. The structural and functional nature of the deciduoma is such that it has been generally accepted to represent a tissue similar to that of the uterine mucosa during early stages of normal pregnancy associated with maternal placenta formation[9-13]. Recent studies have shown that antihistamine agents, when applied topically to the endometrium at the time of traumatization, are effective in inhibiting the development of the decidual cell reaction[14,15,16].

It was considered of interest to determine whether the decidual cell reaction was a "trigger response" which, when once initiated, would go to completion, provided that the proper hormonal status was maintained. The experiments herein reported were carried out to test this, by studying the influence of an antihistamine (Benadryl) administered at various periods after the initiation of an active decidual cell reaction.

METHODS AND MATERIALS

Forty eight adult female albino rats which weighed from 160 to 200 g were used. Daily vaginal smears were taken from all animals. When regularity of the estrus cycle was registered (4-5 day cycle), animals in the proestrus stage were selected and given electrical stimulation of the cervix[17] to induce pseudopregnancy. On the fourth day of diestrus (usually the 5th day after proestrus) the animals were operated on under ether anesthesia to expose both horns of the uterus. Traumatization, in order to provoke decidual growth, was effected by intralumen injection of histamine. One-tenth ml of solution, containing either 1.0 mg of the dihydrochloride or 3.0 mg of the phosphate, was introduced at the base of each horn through a gauge 27 hypodermic needle. In a second group the antemesometrial wall was scratched along most of the horn with a 18 gauge needle.

At various intervals ranging from 0 to 48 hours after the traumatization, animals were operated on again and Benadryl introduced into the experimental horn. Three groups, one receiving 1 mg, one 2 mg, and one 10 mg of Benadryl in 0.1 ml Ringer solution, were studied. In all cases the control horn was injected with Ringer solution.

On the fourth day after initial traumatization, the animals were autopsied and the experimental horn compared with the control. The whole uterus was mounted on a card and fixed in Bouin picro-formol solution.

RESULTS

The results, graphically in Figure 1, reveal that benadryl injected into the uterine lumen in which there existed a developing deciduoma was effective in inhibiting or suppressing the natural growth of the deciduoma even when applied as late as from 18 to 48 hours after the traumatization. Moreover the larger the quantity of Benadryl the greater the interval over which the antihistamine was effective in suppressing the decidual development.

DISCUSSION

The fact that deciduoma induction can be inhibited by an influence applied 18 to 48 hours after traumatization, does not support the notion that the decidual cell reaction is of the nature of a trigger response. The fact that only the decidual cell response in the experimental horn was inhibited suggests, though it does not altogether prove, that the inhibition is a local phenomenon and not dependent on an in-

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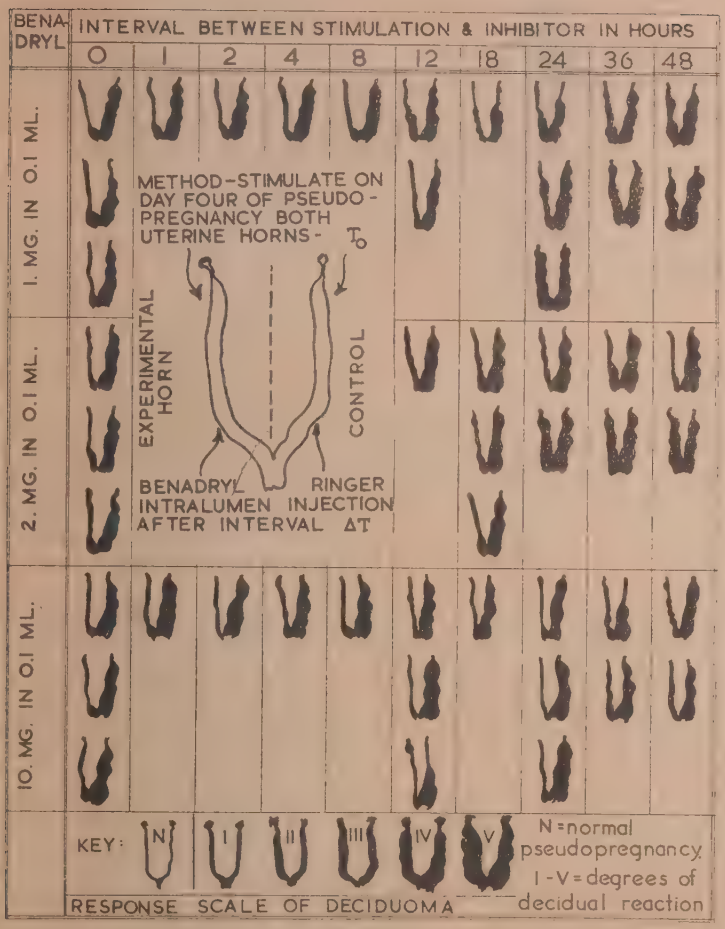

Figure 1

direct action, e.g. through the pituitary or ovary (*cf.* influence of removal of progesterone source, and replacement by estrogens and other steroids[18-21]).

Assuming that these results are also applicable to inhibition of normal placentation, less critical timing would be required than that suggested by previous work[15].

REFERENCES

1. Loeb, L., 1907, *Proc. Soc. Exp. Biol. and Med.*, **4**, 93.
2. Loeb, L., 1908, *Proc. Soc. Exp. Biol. and Med.*, **5**, 102.
3. Frank, R. T., 1911, *Surg. Gynec. and Obst.*, **13**, 36.
4. Corner, G. W. and Warren, S. L., 1919, *Anat. Rec.*, **16**, 168.
5. Long, J. A. and Evans, H. M., 1922. *Mem. Univ. California*, **6**, 1.
6. Krainz, K., 1914, *Arch. Mikro. Anat.*, **84**, 122.
7. Parkes, A. S., 1929, *Proc. Roy. Soc.*, London, **B104**, 171.
8. Wislocki, G. B. and Streeter, G. L., 1938, *Cont. to Embryology*, Washington, **27**, 1.
9. Krehbiel, R. H., 1937, *Physiol. Zool.*, **10**, 212.
10. Williams, M. F., 1948, *Am. J. Anat.*, **83**, 247.
11. Seyle, H. and Mckeown, T., 1935, *Proc. Roy. Soc.*, London, **B119**, 1.
12. Nicholas, J. S., 1942, *Anat. Rec.*, **83**, 457.
13. Nicholas, J. S., 1947, *Quart. Rev. Biol.*, **22**, 179.
14. Shelesnyak, M.C.,1952. *Bull. Res. Counc. of Israel*, **2**, 74.
15. Shelesnyak, M. C., 1952, *Am. J. Physiol.*, **170**, 522.
16. Shelesnyak, M. C., 1952, *Bull. Res. Counc. of Israel*, **2**, 202.
17. Shelesnyak, M. C., 1931, *Anat. Rec.*, **49**, 179.
18. Weichert, C. K., 1928, *Proc. Soc. Exp. Biol. and Med.*, **25**, 490.
19. Courrier, R., 1930, *C. R. Soc. d. Biol.*, **104**, 282.
20. Velardo, J. T. and Hisaw, F. L., 1951. *Endocrinology*, **49**, 530.
21. Hisaw, F. L. and Velardo, J. T., 1951, *Endocrinology*, **49**, 732.

THE CONCEPT OF BIOTIC ORGANIZATION IN SYNECOLOGY

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I. ECOLOGICAL AND PHILOSOPHICAL APPROACH

Nearly every modern textbook of ecology stresses the highly integrated supraorganismic structure of communities, giving the impression that this concept is the established basis of ecology, induced by the analysis of biocoenoses. This concept, backed by established authority, is generally regarded, if not as a fact, then at least as a scientific hypothesis not less firmly founded than the theory of transformation. Even superficial analysis, however, shows the foundations of this hypothesis to be less stable than might be supposed.

Three essentially different approaches have been made to the problem.

1. *The unity of the universe or the general approach.* A. J. Lotka[1] is the outstanding protagonist of this point of view and stresses the physico-chemical unity of the universe. He conceived physical biology as a branch of the general mechanics of evolution and points out that the mechanics of systems undergo irreversible changes due to the distribution of matter amongst their several components. Although, aided by statistical techniques, Lotka elaborated the data by inductive reasoning, in his book emphasis is upon deductive methods of mathematical analysis "as applied either to data furnished by observations, or to 'unknown' quantities, blanks, as it were, in our formulae, ready for numerical substitution whenever concrete data become available". (p. 54).

The circulation of the elements and the form in which the elements of special biological importance take part in this circulation are stressed. Lotka ends his book with this outlook upon man's position in the unity and in the circulation of the universe: 'This is the goal of evolution (of man), the perfect adjustment of feelings to actions, which guarantees survival; to say with the great Stoic: "O Universe, whatsoever is in harmony with thee, is in harmony with me." The being whose will is so adjusted is Fortune's favorite; all things must bend to his will as they bend to Nature's law. For his will is Nature's law'.

Similar views of the functional unity of the universe have often found expression in philosophy, where again they are professedly based upon deduction or intuition. Such a view has recently been expressed by van Leer[2]: 'To understand fully the organic oneness (of the universe), we must have it clear in our mind what an organism really is: An organism is the conception of the functioning together as a whole of different constituent parts. All parts derive their true significance from the fact that they are properly functioning parts of the organism, while the organism itself is what it is by virtue of its parts. The organism being actually only the integration of the functions of the parts and being therefore as an entity in itself merely a conception of the mind, nevertheless exists in full reality. We positively know it to be, and to be intrinsically different from and of much greater potency than the sum total of its parts. Every part in the organism makes its indispensable contribution and has to perform its function properly in order to be fully itself. But in doing so it is not serving its own purpose only; it creates and maintains at the same time the whole... Divorced from the body, (the parts) lose completely their identity and character... In the entirety of creation everything is an organic entity in itself but has as such no meaning. It derives significance, it can be whatever it is meant to be, only as a functioning part in another entity, this entity in its turn deriving significance only as part in another entity, and so on and so forth till the multiplicity of relations of the whole merges in God's all-embracing oneness... The human being who is conscious of the organic unity of everything and is keenly aware of what an organism really is,undergoes a radical change in his attitude to life and to his fellow men He knows that all things derive their character, their identity, *are* whatever they are meant to be, only by virtue of their function in a certain unit. It is this awareness of relation and man's consciousness that he knows about it which distinguishes man from everything else in creation and makes him human in the highest sense.'

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Similar trends are expressed in the school of emergent evolution, and even the general definition of ecology undergoes a change in this direction. We get farther and farther away from the earlier definition, that ecology is the study of the influence of the animate and inanimate environment upon the organism or a given species of animals or plants. Everything being a function, the organism, population or species becomes a function within higher organic functions. If not fully meant in this sense, this is nevertheless the conclusion to be drawn from statements like that of M.E. Solomon[3]. In an analysis of the control of natural populations he writes: 'The population functions in relation to a whole which includes itself. It is therefore better to think of the population as an integral part of the ecosystem. If we wish to consider the population as an entity in relation to its ecological setting, that setting should be the ecosystem, rather than an imaginary 'ecosystem minus the population', called the environment.' Each of these theories of the generalized approach is very captivating, and is a most stimulating hypothesis, yet none claims to be the result of scientific method, the outcome of inductive and factual synthesis.

2. *The supraorganismic approach in synecology.* Even before the definition of the concept of biocoenosis, that is of life-communities by Moebius[4], it was realized that a certain, sometimes conspicious, dependency exists between many partners of a bio-community. Such relationships manifested in food-chains, chains of development, food-pyramids, growth-curves of populations, oscillations between prey and predator, and so on, have become much more frequently studied in recent times. Such relations are a commonplace, yet the aim of the organismic biocoenosis hypothesis exceeds by far the mere description of empirical fact. The interrelations, compensations and regulations between a species and its food, competitors, enemies and diseases, and many other factors must be considered as far reaching integrations which permit one to regard the bio-community as a kind of supraorganismic structure This view, is illustrated in the following quotations from two (typical) modern textbooks:

F. E. Clements and V. E. Shelford[5], the great American pioneers of synecology, state: 'One of the first consequences of regarding succession as the key to vegetation was the realization that the community is more than the sum of its individual parts, that it is indeed an organism of a new order. For this reason, it was considered to be a complex organism, bearing something of the same relation to the individual plant or animal that each of these does to the one-celled prototype or protozoan. The novelty of this proposal naturally evoked criticism..., (yet) by an increasing number (it) has come to be regarded as constituting a new base for almost unlimited development. However, it is essential to bear in mind the significance of the word 'complex' in this connection, since this expressly takes the community out of the category of organisms as represented by individual plants and animals' (p.21). 'Like those of the individual, the functions of the community are not only most intimately connected with one another, but they are also involved in a complex of activities in which their simple causal relation is obscured or completely lost to sight.' (p.66).

In 'Principles of Animal Ecology[6]' the supraorganic structure of the bio-community is regarded to such extent as a proved fact that no other point of view is described by the authors. We find only two hints that an opposite view is to be found elsewhere (p.508 and 721). They state: 'The major community may be defined as a natural assemblage of organisms which, together with its habitat, has reached a survival level such that it is relatively independent of adjacent assemblages of equal rank; to this extent, given radiant energy, it is self-sustaining ...The formation of the community may be considered as a result of ecological selection, in which the building blocks, or organisms, unable to exist alone, fall into place to produce a self-sustaining whole of remarkable complexity. Organization of such an accumulation is obligatory, and the universality of the community is the proof of this general proposition. The functional integrity of the community is a logical extension of the facts examined, since it becomes apparent that the community must be the natural unit of organization in ecology, and hence is the smallest such unit that is or can be self sustaining... Thus cells, organisms, populations, societies, and communities are progressively complex biological systems. All five are protoplasmic, interdependent integrations in the struggle for nourishment and other interrelations. Their protoplasmic nature is obvious, but the complex interdependence of organisms and their arrangement into organized communities for survival is only now becoming realized. This realization suggests an extracellular extension of the Cell Doctrine. (p.436ff.) For 17 different functions the comparison of cell, multicellular organism and community is given in a most interesting table (p.440) where the parallels are stressed, to show the organismic structure of the communities.

Great emphasis is laid upon the fitting of this bio-community concept into the evolutionary pattern. 'Interaction between different species of organisms and interactions between organisms and their environment produce selection pressures. Reciprocal genetic patterns evolve by means of such selection and produce interspecies adaptations, interdependence, and integration. Harmful *disoperation* between species eliminates itself. Exploitation tends to evolve toward toleration and mutualism. The evolution of mutualism between species has not progressed so far as cooperation between parts of an individual or between individuals in an intraspecies population. The evolution of division of labor and integration between species results in a biotic system that may appropriately be called an interspecies supraorganism. The incorporation and control of the physical habitat by the interspecies supraorganism produces a unitary ecosystem. *Homeostatic* equilibrium within the ecosystem (balance of nature) is largely the result of evolution' (p.728).

Here we have a detailed attempt to apply the hypothetical neo-mendelian mechanism of evolution, the struggle for life and the survival of the fittest being replaced by survival value, population- and mutation-pressure, etc. from multicellular organisms to bio-communities. This bold attempt is, of course, even less valid than the neo-mendelian theory of speciation which is being severely questioned at present even by some genetists and caution is expressed by some of the actual promoters of the supraorganismic theory. In an interesting paper Emerson[7] writes: "Possibly we should classify ecological associations as ascending levels of super-organismic integration which show partial physiological isolation between the community types, and complete isolation only between the biota of this planet and that of some other planet. The integration of all life on the earth forms a 'Leviathan' (Patten 1920), and the analysis and synthesis of the mechanisms of this 'Leviathan' are the major duty of the ecologist. Let us not, however, raise the superorganismic concept to an "all or none" principle. Let us rather use the perspective it gives us to stimulate further study and understanding."

3. *The empirical approach to synecology.* The present writer is perhaps the most outspoken champion of this approach.[8] We reformulate here our approach in a slightly modified form.

The bio-community as an empirical or statistical conception is compatible with the descriptions, deductions, and conclusions of all those workers who have made surveys of their own in the field. It is compatible with the original and most widely accepted definition of biocoenosis as a 'population system in labile equilibrium which appears at certain ecological conditions' (Resnoy) as well as with the oldest definition of the biocoenosis by Moebius[4]. This conception is compatible with the observed fact that the vegetation and the fauna of any landscape have general traits in common. In a desert where lack of water and low humidity predominate, all biological processes are dominated by them (pigmentation, habitats, habits, seasonal and diurnal activity, etc.). The same is true of animals living in the abyssal, pelagial, littoral of the sea or in the tundra or a tropical rain-forest. The 'genius loci' (Caradja) of each major habitat is expressed by common traits in sociability, body-size, breeding-stratum, colouring, etc.

We may define bio-communities as a combination of plants and animals, recurring in an approximately similar composition, at least with regard to dominant and characteristic species, wherever similar ecological conditions exist within the same biogeographical territory. Similar habitats in different biogeographical regions show a surprising analogy and homology in the composition of their life-communities. This convergence is the outcome of selection: negative selection by the environment, positive selection by similar taxes and behaviour. Within the bio-communities interactions occur between various species of plants and animals, but even the beginnings of any real integration of the members of the biotic community, the biocoenosis, into a supra-organismic structure have never been demonstrated. As a rule, each species exists within the community in its own right, which is expressed by the different territories of every species as conditioned by its own reaction basis, different from that of all other species. Little active co-operation occurs in the animal community; more often we find a certain mutual tolerance of such species, whose niches overlap partially. Thus, the bio-community is a useful empirical and statistical concept, facilitating the description of plant and animal life in the various habitats, but not a dynamic, supra-organismic structure. As we will show later on, certain such bio-communities show a definite lack of organismic behaviour, with regard to growth, metabolism and longevity. The supraorganismic theory is an intuitive hypothesis, but not an inductive synthesis.

Similar empiristic views have been expressed by R. Lindroth-Lund and by some members of the Finnish school of ecology.

II. EPISTEMOLOGICAL APPROACH

Kant, the founder of modern epistemology, states in his Critique of Pure Reason[9]: "Experience is by no means the only field to which our understanding can be confined. Experience tells us what is, but not that it must be necessarily what it is and not otherwise. It therefore never gives us any really general truths; and our reason, which is particularly anxious for that class of knowledge, is roused by it rather than satisfied. General truths, which at the same time bear the character of an inward necessity, must be independent of experience—clear and certain in themselves".

This absoluteness, these general truths are certainly not gained from separate sensations and events, which may alter their sequence in the future. The necessity for these general truths is derived from the inherent structure of our mind. "For the mind of man is not passive wax upon which experience and sensation write their absolute and yet whimsical will; nor is it a mere abstract name for the series or group of mental states; it is an active organ which moulds and coordinates sensations into ideas, an organ which transforms the chaotic multiplicity of experience into the ordered unity of thought . . . Space and time are not things perceived, but modes of perception, ways of putting sense into sensation; space and time are organs of perception, as is cause. These three are modes of perception and conception, which must enter into all our experience, since they are the web and structure of experience; these dilemmas arise from supposing that space, time and cause are external things independent of perception. We shall never have any experience which we shall not interpret in terms of space and time and cause; but we shall never have any philosophy if we forget that these are not things, but modes of interpretation and understanding."[10]

In his Critique of Aesthetic Judgment[11], Kant remarks that the appearance of external design is not a conclusive proof of Providence. The scientists who have abandoned this idea should use it, as there is undoubtedly design; but it is internal design, the design of the parts by the whole. If science will interpret the parts of an organism in terms of their meaning for the whole, it will have an admirable balance for that other heuristic principle—the mechanical conception of life—which also is fruitful for discovery, but which, alone, can never explain the growth of even the blade of grass.

And in the part on Transcendental Analysis of the Critique of Pure Reason we find the base for Hegelian thought, namely that the laws of thought are also the laws of things, for things are known to us only through this thought that must obey these laws, since it and they are one: the laws of logic and the laws of nature are one, and logic and metaphysics merge. "The generalized principles of science are necessary because they are ultimately laws of thought that are involved and presupposed in every experience, past present, and to come. Science is absolute, and truth is everlasting".[12]

We may compare these conclusions of Kant with a selection from those expressed in one of the most modern philosophical analyses of epistemology, with Bertrand Russell's Human Knowledge.[13] He defines knowledge as a vague concept due to the vague meanings of a word, except in logic and in pure mathematics, and as all that we count as knowledge is in a greater and less degree uncertain (p. 113). Brouwer's *intuitism* which holds that a some-sentence may be neither true nor false, is however refuted (p. 158). Knowledge is actually a matter of degree. "The highest degree is found in facts of perception, and in the cogency of very simple arguments. The next highest degree is in vivd memories. When a number of beliefs are each severally in some degree credible, they become more so if they are found to cohere as a logical whole. General principles of inference, whether deductive or inductive, are usually less obvious than many of their instances, and are psychologically derivative from apprehension of their instances" (p. 174).

It is interesting how Russell introduces "the greater weight of authority" into the discussion of knowledge, pointing out, that in the vitalism-mechanism discussion the greater authority is on the side of mechanism (p. 215). Analysis of structure, however complete, never tells all that we wish to know about an object, nothing about the relations of the object to objects that are not parts or components of it (p. 268).

"It is customary to speak of induction as what is needed to make the truth of scientific laws probable. I do not think that that induction, pure and simple, is fundamental . . . Every finite set of observations is compatible with a number of mutually inconsistent laws, all of which have exactly the same inductive evidence in their favour. Therefore pure induction is invalid, and is, moreover, not what we in fact

believe . . . The law is one which had suggested itself more or less independently of the evidence, and had seemed to us in some way likely to be true. When this is the case, subsequent confirmatory evidence is found astonishingly convincing" (p. 330).

Of great importance is the following: "Science is concerned to infer laws from particular facts. An inference of this sort cannot be deductive, unless, in addition to particular facts, there are general laws among our premisses; as a matter of pure logic this is fairly evident. It is sometimes thought that, though particular facts cannot make a general law *certain*, they can make it *probable*. Particular facts can certainly *cause* belief in a general proposition: It is our experience of particular men dying that has caused us to believe that all men are mortal... Certain kinds of particular facts are evidence of general laws. And since deductive logic knows no such principle, any principle which will justify inference from the particular to the general must be a law of nature, i.e. a statement that the actual universe has a certain character which it would be possible for it not to have" (p. 354).

"Mathematical intuition is by no means infallible as regards to inductions, but in the case of good mathematicians it seems to be oftener right than wrong. I do not know how to make explicit what guides mathematical intuition in such cases. Meanwhile, we can only say that no known limitation will make induction valid as applied to the natural numbers" (p. 422). "I incline to think that valid inductions, and, generally, inferences going beyond my personal past and present experience, always, depend upon causation, sometimes supplemented by analogy" (p. 470).

Russel concludes: "The forming of inferential habits which lead to true expectations is part of the adaptation to the environment upon which biological survival depends. But although our postulates can, in this way, be fitted into a framework which has what we may call an empiristic "flavour", it remains undeniable that our knowledge of them, in so far as we do know them, cannot be based upon experience, though all their verifiable consequences are such as experience will confirm. In this sense, it must be admitted, empiricism as a theory of knowledge has proved inadequate, though less so than any other previous theory of knowledge. Indeed, such inadequacies as we have seemed to find in empiricism have been discovered by strict adherence to a doctrine by which empiricist philosophy has been inspired: that all human knowledge is uncertain, inexact, and partial. To this doctrine we have not found any limitation whatever" (p. 526).

We end this series of epistemological quotations with one by A. Standen[14], who has recently analysed the bases and functions of modern science. Of Biology he writes, that it is "one vast mass of analogies, very different indeed from the cold logical thinking of the physicist. Some of the higher reaches of biology, such as genetics, biochemisry, neurophysiology, (ecology), and other 'ologies', are difficult and exacting studies, and those who practise them can rightly claim that they do some making of hypotheses and testing them against experiment, although even there they are apt to talk of 'understanding in terms of', or 'developing the concept of' or 'stressing this, or that, aspect'. In its central content, biology is not accurate thinking, but accurate observation and imaginative thinking, with great sweeping generalizations. The 'Unity of Life' is a catch phrase biologists are addicted to, although this can hardly be regarded as confirmed by experiment, because it is almost impossible to say what it means, if indeed it has any meaning at all." (p. 72). And elsewhere (p. 142) Standen flatly states, that neither science nor scientists have any notion what goes on in the zone of higher knowledge.

No ecologist—after having read these quotations —will deny that they have a very direct bearing upon the problems and methods of synecology[15]. Whilst all three authors differ considerably concerning their general conclusions, they all insist that only intuitive inferences, derived from a stock of observations and experiments and determined by the innate modes of operation of the human mind lead to generalisations and that induction by itself is always unable to lead to higher principles, rules and laws.

III. DISCUSSION

The supra-organismic concept has found its most enthusiastic support in two fields of ecology, those of limnology and social animals.

S. A. Forbes[16] wrote as long ago as 1887: "(The lake) forms a little world within itself - a microcosmos within which all the elemental forces are at work and the play of life goes on in full, but on so small a scale as to bring it easily within the mental grasp'. And A. Thienemann[17] has unceasingly advanced this idea, "Every life community forms together with the environment which it fills, a unity,

and often a unity so closed in itself, that it must be called an organism of higher order", even if all life communities form part of the great vital space of the earth as a whole.

Thienemann has often stressed the supra-organismic character of the lake from a dynamic, or, better, from a physiological point of view. Considering the total circulation of organic and inorganic matter within a closed system such as a pond or a lake, a certain analogy to the metabolsim of an organsim may be discovered. But this circulation of matter in a closed, autarctic system – apart from aeration and sunlight, common to almost all life communities – is nothing more than an analogy. It simply means that the nutritional salts are used for the production of the autotrophic flora, which is being used in turn by smaller animals which serve as food to fish. All remnants are decomposed by bacteria, and their matter again enters the circle of production either as *detritus* circulated by detritus-feeders or as nutritional salts utilised by the autotrophic flora. This system is therefore not to be compared with the metabolism of an organism which requires purposely and selectively the materials necessary for the maintenance of the organism from outside, and which has a complicated physiological system of internal dissimilation, assimilation, transport, and distribution of matter. One phase of the circulation interrupted, the organism breaks down. However, in the lake, life, perhaps in the form of another life community, would be maintained if no fish were present or if bacterial decomposition were quite incomplete. The only conclusion to be drawn is that here also the relations of the food pyramid are maintained. An empty food space within a harmonic environment always calls for a filling up with suitable organisms from the neighbouring biotopes. The mere fact of the maintenance of the food pyramid cannot be regarded in this case as a proof for supra-organismic organisation of the bio-community[18]. A strong additional argument against this concept is the mode of establishment and longevity of such a biotope which depends entirely on the stability of the environment. In the stable environments of the abyssal, pelagial, benthal zones of the sea conditions are fairly stable over long, sometimes even over geological periods, wheras the littoral community exposed to the rise or fall of the sea, the erosive effect of the tides, etc. is entirely unstable. Once the conditions change, the life communities follow quickly. Shelford[19] states for the *Balanus-Littorina*-biome on rocks as well as for the *Macoma-Paphia*-biome on sandy beaches, that they develop within a few months. "All the communities studied are characterized by short life-histories (of the representative species) and rapid replacement: hence, also rapid development and quick response of community composition to minor changes in external conditions." The identification of the bio-community of the lake by metabolism, mode of establishment, and longevity (dependent also on changes in the environment produced by the activity of the organisms) is thus mere analogy, but not homology.

In social animals the beginnings of integrations may lead to a higher degree of real supraorganismic organisation. We will omit here any discussion of man. In many monospecific communities, such as the families of social insects no doubt is possible to attain the high level of supraorganismic integrations [20,21] with regard to division of labour and its adjustments under experimental conditions, mode of reproduction of the families, develoment and longevity, social temperature regulation, and and so on. These integrations are in many cases so farreaching that they are, so far, the only category of life communities for which a real homology to the organisation within multicellular organisms can be established.

It is, in general a weak point of ecology that it is mainly based upon analogies between two sets of phenomena. What is really disturbing is the ease with which new analogies are built up, once the accidental character of any such analogy is discovered. Physiological foundation by experiment or by counts of area-samples are the first beginnings for the development of proper and specific methods in ecology, both still far too rarely applied.

The harmony of living nature has occasionally roused an almost religious enthusiasm amongst ecologists, almost comparable to that of the age of Jan Swammerdam when biological and microscopical research was regarded as the study of the wonders of God's creation. German ecologists have compared the supraorganismic hypothesis of the bio-communities to listening to the 'symphony of the spheres', a well chosen simile stressing the intuitive character of this theory. It is obvious that no scientific method can arrive at a perception of this symphony of the spheres. It is in this sense, and in this sense only 'that we would gladly accept the accusation of being a non-musical person, unable to perceive the music of nature's composition'.[22]

To this S. L. Tuxen[23] remarks: 'To accept beforehand what is not 'probable to-day', seems to me

to be a sterile procedure; even if these *coactions* were mere ripples at the surface, it is more useful to assume that they are of far-reaching importance, if we are to investigate them, than to reduce them at the outset to mere trifles. Altogether it will be more useful to many investigators to have a picture, a 'vision', before them before they set to work, even though it may be wrong, than to work in such a way that each result merely gives rise to the next problem... It seems to me that if 'musical' in this connection is to be regarded as identical with the ability to enter intuitively into the subject-matter, it means a serious defect to admit that one lacks this ability.'

Thus, Tuxen is one of the few modern ecologists who does not pretend that the supraorganismic biocoenosis is a proved fact, but honestly calls it a vision stimulating synecological research. We agree with Tuxen's opinion, and it is only to point out where we actually differ, that these lines have been written.

The crux of the problem is the widely spread lack of epistemological understanding in biological thinking, already deplored by Lotka[24] and many others. No partisan of the empiric school has to our knowledge ever denied the possibility of a supraorganismic structure of bio-communities. This school has only stressed that at the present state of our knowledge the factual basis of the analysis of the 'web of nature' is entirely inadequate for a general synthetic solution. Scientific method proceeds from description, observation, measuring, counting, weighing and similar methods to an inductuion which is evolved from the sum of available facts and observations. From such a purely methodological point of view it is impossible to give any picture and decision on the inherent structure, if such exists at all, of the bio-comminities. We agree, however, entirely with Tuxen that any heuristic theory is better than nothing as guidance for research and scientific analysis. This has been realised from Aristotle[25] to Singer[26]. The former has stated: 'Such appears to be the truth about the generation of bees, judging from theory and from what are believed to be the facts about them; the facts, however, have not yet been sufficiently grasped; if ever they are, then credit must be given rather to observation than to theories, and to theories only if what they affirm agrees with the observed facts'.

We remember too well the enormous stimulating effect which the theory of the biological equilibrium between hosts and parasites[27] had upon the development of ecology as well as of applied entomology, than to belittle the value of any general heuristic theory. What we refute is the claim of any such theory, and especially one still so vague as the supraorganismic structure of bio-communities, to truth. We accept it gladly as a heuristic principle, stimulating and fascinating, which, like all generalisations followed up to their last consequences, will not only elucidate its own degree of truth or fallacy, but will bring out a great number of facts and relations which otherwise would not so speedily have been discovered. We gladly accept thus the supraorganismic community concept as a most valuable heuristic principle but we refute its claim to be an established fact. The general consensus of the ecological authorities of our day shows that their intuition, built upon the subconscious digestion of the observations of their *lifetime*, strongly suggests and supports their view. Only history will show, if this consensus belongs to the true intuitions of Russell or is a fashion of our time or is eventually based upon the unifying and simplyfying mode of operation of the human mind.

The human mind has an inborn tendency, we may perhaps even say need, for the simplification of the complex, for the unification of the diverse, of the phenomena of nature as well as of other fields of human thought. The supraorganismic biocoenosis is merely an anticipation of results. It is believed, yet not proved. This does not mean that it is false or untrue, but only that so far it is an aprioristic anticipation of our mind which may be right or may be wrong. Kant points out that such anticipations of our mind are one of the important ways of cognition of the human mind. If consensus of the authorities is a proof for truth, then it is right. We have, anyhow, no reason *not* to believe in the supraorganismic character of life communities, as long as it is clear that it is based upon *intuition*, and not upon scientific method. The only demand and restriction must be an agreement that it is based upon another road of cognition than observation and experiment.

The pure scientific method of induction cannot, as Russell points out, reach the realms of higher knowledge, of complete synthesis of general principles. True scientific synthesis comes not from induction but from intuition or deduction. The latter remain, however, theories which require confirmation by inductive experience. Their intrinsic value depends upon the number of non-connected (prima facie) phenomena which they explain and, of course, that—even if part of the pertinent phenomena are left unexplained—they shall not be in contradiction with any one of them. Outstanding illustrations of valuable theories are the transformation of species, the chromosomal base of heredity, the cell-theory,

none of which is today — except perhaps the first — without serious criticisms and discussions. Yet all three of them have in a limited or changed form a good chance to survive our generation. That the same can be asid about the supraorganismic biocoenosis is much more doubtful.

The present day phase of this theory does not give any functional explanation beyond mere analogies. There is no link between the observed facts and the theory. None of the assumed links surpass fractional chains of relations (food-chains, life-cycles, food-pyramid, etc.). Too simple interpretations are certainly bound to failure. Interspecific relations within the biocommunity definitely do not form a well balanced system in which every minor change of composition has far reaching consequences for the structure of the entire community, such as the healing even of a minor wound signifies for the entire organism. Buffering by automatic adjustments[28] as well intercompensatory tendencies[29] occur as widely established principles. They counteract the effect of minor changes within the bio-community and tend to give it the observed stability. Yet similar phenomena are known from physical and chemical systems and hence do not call for explanation by supraorganismic structure.

J. Pelseneer[30] tries to demonstrate that there exists no general scientific method at all and that scientific progress is maintained by the artistic temperaments amongst scientists. The background of this well pointed thesis is, of course, the same which Russell expressed in another way: that mere induction does not lead to new guiding principles, but only intuition and deduction. This brings us to our main thesis: There are more scientific roads to knowledge than one. Scientific induction gives us well measured and secured facts. The theories which are the soul of science are, however, gained by intuition and deduction. Both roads are admissible and of basic value. The only mortal sin is to anticipate theories as established facts when the inductive material may suffice to stimulate an inspiring vision, but do not—or not yet—form a solid base for truth or even for a high degree of scientific probability. Tuxen has well said that it is a poor science which renounces visions, but it is a still poorer science which commits this mortal sin. Science advances only when it passes between this Scylla and Charybdis into the open sea of balanced judgment between both these methods.

IV. CONCLUSIONS

1. The theory of a general circulation of matter and energy in the universe (Lotka) as well as that of a functional unity within the entire universe (as maintained by many philosophical schools in past and present) are consistent hypotheses, in every case based upon intuition or deduction. They give no primary support to the supraorganismic character of bio-communities.

2. The inductive basis of observation and experimentation in synecology offers no direct connective link with this intuitive theory. The general support for it obviously depends upon an aprioristic anticipation of our mind, largely due to the mode of operation of our mind striving for unity in the diversity of phenomena (Kant).

3. The scientific approach demands that these different kinds of cognition must be clearly separated, as long as they are not firmly linked by supporting evidence. The statistical fact that similar bio-communities are established in homologous environments all over the world and that they are stable as long as their environments remain stable can be explained in other ways than by the supraorganismic theory.

4. This is by no means to say that this theory is wrong. It simply means that as long as the bridging evidence between induction and intuition is missing or weak, no theory can be accepted as an established fact. Strict separation of concepts built upon scientific method and those obtained by intuition or deduction is required in order to appreciate the actual value of any theory.

5. The main reason that these different approaches to truth are in science so often obscured and confounded is obviously the lack of training and interest in epistemology, which today is more than ever needed for every scientists.

REFERENCES

1. Lotka, A. J., 1925, *Elements of Physical Biology*. Baltimore, 49. 54, 252, 434.
2. Leer, P. van, 1925, *The Vision*. Jerusalem, 14 ff., 24.
3. Solomon, M. E., 1949, *J. Animal Ecol.*, **18**, 10.
4. Moebius, K., 1877, *Die Auster und die Austernwirtschaft*, Berlin.
5. Clements, F. E. and Shelford, V. E., 1939, *Bioecology*. New York, 20, 66.
6. Allee, W. C., Emerson, Park, Park and Schmidt, 1949, *Principles of Animal Ecology*. Philadelphia and London, 436ff., 728.
7. Emerson, A. E., 1939, *The American Midland Naturalist*. **21**, 201.
8. Bodenheimer, F. S., 1938, *Problems of Animal Ecology*. Oxford, Chapt. V.
9. Kant, I., *Critique of Pure Reason*, Macmillan, 1.

10. DURANT, 1929, *The Story of Philosophy*, New York, 291, 294, 296, 298.
11. KANT, I., *Critique of Aesthetic Judgment*, Oxford, Sect. 29.
12. DURANT, W., *l.c.*, 304.
13. RUSSELL, B, 1948, *Human Knowledge*. London.
14. STANDEN, A. 1952, *Science is a Sacred Cow*, London and New York.
15. BODENHEIMER, F. S., *Problems*, 144.
16. FORBES, S. A., 1877, The Lake as a Microcosm, *Bull. Peoria Scient. Assoc.*
17. THIENEMANN, A., 1925, *Die Naturwiss.*, **13**, 589—591; 1950, *Oikos*, é, 149—161.
18. BODENHEIMER, F. S., *Problems*, 137ff.
19. SHELFORD, V. E., 1932, *Ecology*, **14**, 105—120.
20. EMERSON, A. E., *l.c.*, 182—209.
21. BODENHEIMER, F. S., 1937, *Biol. Reviews*, **12**, 393—430; 1937, *Quart. Rev. Biol.*, **12**, 406—425.
22. BODENHEIMER, F. S., *Problems*, 142.
23. TUXEN, S. L., 1944, *The Hot Springs, their Animal Communities and their zoogeographical significance*, Copenhagen and Reykjavik, 173.
24. LOTKA, A. J., *l.c.*, 4 ff.
25. ARISTOTLE, 1912, *De Generatione Animalium*, 760b, Oxford Translation, 5, Oxford.
26. SINGER, C., 1950, *History of Biology*, New York, 17.
27. HOWARD, L. O. and FISKE, W.F., 1911. The importation into the U.S. of the parasites of the Gipsy Moth, *Bull. U.S. Dept. Agric.*, Entom., No. 91.
28. ERRINGTON, P. L., 1951, *The American Naturalist*, **85**, 273—292.
29. SOLOMON, M. E., *l.c.*, 1—15.
30. PELSENEER, J., 1953, Y a-t-il une methode scientifique? *Transact., 7th Int. Congress Hist. Sci.*, Jerusalem, (in press).

SEASONAL VARIATIONS IN SPERMATOGENESIS OF SOME FARM ANIMALS UNDER THE CLIMATIC CONDITIONS OF ISRAEL*

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The seasonal fertility factor involves considerable difficulties in farming economy, especially in the matter of uniform milk supply. Various nutritional, veterinary and other methods have been tried, with a view to overcoming these difficulties. However, in spite of all such attempts, most farm animals retain a more or less pronounced breeding season.

The farm animals which had been bred in the country for centuries and which relied on the natural vegetation for sustenance, were incapable of suplying the needs of the modern settler, with his high living standard. To ensure better returns, it has been necessary to import stock from advanced, mostly northern countries, where climate is much cooler than in Israel. It is not, therefore surprising that impaired fertility is often associated with imported animals and their offspring.

Marshall[1] demonstrated that an animal's breeding season changes when it is transferred to the other side of the equator. He related this phenomenon to the alteration in photoperiodic conditions. Bonsma[2] found reduced fertility in males of selected breeds which had been transferred to hot countries, as a result of excessive heating of the testes: the degree of disability depending on the thickness of the scrotum. An account of investigations by other workers, as given by Philips[3], suggests that the woolly covering of the scrotum plays an important part in the inhibition of spermatogenesis, while other workers assign to the scrotum an important function in regulating the activity of the testes and protecting them from excessive heating. It has been established that complete sterility results when the testes are maintained at the temperature of 41°C for 100 hours. The atrophy of the semeniferous tubules resulting from direct warming of the testes closely resembles degeneration symptoms brought about by high ambient temperatures and referred to as "summer sterility". Bogart and Mayer[4] attribute summer sterility to inactivity of the thyroid gland. Schindler[5] found in imported as well as in Israel-bred bulls of pure Dutch and Holstein-Freesian breed a period of semen-deterioration, as expressed in reduced viability of the spermatozoa and a low rate of conception. These manifestations can be attributed to the effect of high temperatures of the environment on animals originating from cooler climates.

It can be assumed that the sexual behaviour of native farm animals which have been bred in this country for centuries, has adapted itself to the environment. A study of such ecological adjustments might throw some light on the problems facing the animal breeder.

The investigations were concerned with changes occurring in the conditions of the seminiferous tubules and an attempt has been made to correlate the histological observations with sexual behaviour. In order to ascertain the relative effect of summer heat and other factors on the activity of the testes, males were selected from several kinds of farm animals, whose mating seasons do not coincide. It should, however, be noted that the calving season of all the kinds investigated is about the same — winter and early spring, i. e .the time when under natural conditions the suckling mother and the young can avail themselves of plentiful fresh herbage. It must be remembered that in Israel the supply of green succulent feed is confined to the months of December to April, while during the remainder of the year the animals can graze mostly on dried vegetation and straw. There is no doubt, therefore, that if parturition were to occur in the summer, the mother's milk supply would not be adequate to sustain healthy offspring. It can thus be assumed that these nutritional factors have tended, by means of natural selection, towards a shortening of the breeding season, as a form of adaptation to the environment.

Although it is fully realized that the ovaries activity play an important part in determining the breed-

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ing season the present report is concerned with spermatogenesis and is primarily based on a study of changes occuring in the seminiferous tubules.

Samples of testes and epididymis collected in slaughter-houses from mature and healthy males provided material for histological examinations.

CAMEL

In the camel both mating and parturition occur during the cold winter months. The male's scrotum is relatively small and is closely attached to the body. In the winter-rut period the testes grow considerably in size; during the hot summer-months they recede between the hind legs towards the abdomen. There are apparently instances when the testes penetrate partly into the inguinal canal. The variation in the weight of testes as between the active and the inactive stage amounts to about 30 per cent (averages of 96 and 66 g respectively). As opposed to the other animals dealt with in this paper, the camel shows no interest in the female during the summer.

The diameter of the seminiferous tubules contracts from an average of 183μ in the months of sexual activity to 130μ during the inactive season. During the period of sexual inactivity one or two layers of cells with resting nuclei can be discerned in the tubules; there are no spermatozoa in evidence and the lumen of the tubule is filled with liquid in which fragments of cells are suspended (Figure 1). A very small number of disintegrating spermatozoa can be found in the epididymis (Figure 2). The overall histological picture resembles that described in rams affected by summer sterility.

During the season of sexual activity the semeniferous tubules swell out until they are closely packed together, while the number of cell-layers increases to 5—6. The nuclei are in a state of active division and numerous spermatozoa can be observed — partly submerged in the Sertoli cells and partly aggregating around the periphery of the lumen, with their tails pointing towards the centre (Figures 3 and 4).

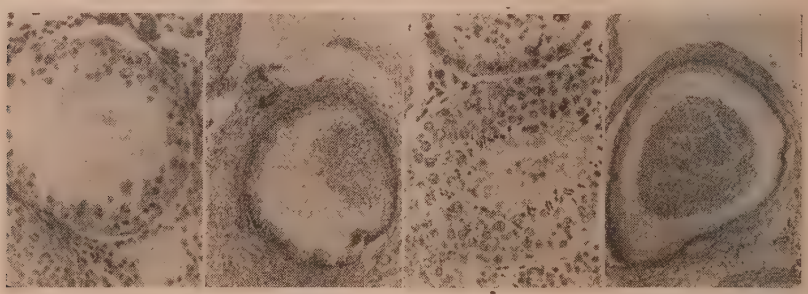

Figure 1 Figure 2 Figure 3 Figure 4

CAMEL — Cross Sections : 1) testes tubule in September during rest period 2) epididymis in September -lumen empty 3) tubule in February at the peak of activity 4) epididymis in March—lumen filled with spermatozoa

The seasonal cycle of spermatogenesis in the camel can be roughly divided into four periods: (a) November-January; regeneration; (b) February-April: maximum activity; (c) May-July: disintegration of cell-layers and deflation of the tubules; (d) August-October: rest-period accompanied by symptoms of summer sterility. The regeneration of the tubules sets in some two months before the beginning of the mating season. On the whole, the rate of degeneration considerably exceedes that of the regenerative process.

It seems that the seasonal changes in spermatogenesis are largely determined in the camel by the high ambient temperatures prevailing in the summer.

BULL

The native Arabian bull mates normally in spring, from March until May. During the remainder of the year the bull shows sex excitement when confronted with a cow which happens to be in heat, but it is doubtful whether he is potentially fertile on such occasions; it is probable that out-of-season matings are generally unproductive. It is a fact that parturition is confined to a definite short period. Arabian cattle bred on Jewish farms and adequately fed, does not show any marked deviation from the normal

breeding periods. It can therefore be concluded that the sexual cycle is largely determined by hereditary factors and not by nutrition or management.

Histological examinations of the testes and the epididymis in the Arabian bull indicate conspicuous seasonal changes in the conditions of the semeniferous tubules. Until May there is intense activity and cell-division in the tubules, suggestive of high fertility (Figure 5), while in early summer (June-August) typical symptoms of summer sterility can be detected in most bulls (Figure 6). From August till December one can discern in the whole or in parts of the testes, additional changes which differ from those characteristic of summer sterility. The condition resembles that described by Erbs *et al*[6]. (Figure 7) as symptomatic of vitamin A deficiency. The assumption that avitaminosis A may be responsible for the degeneration of semeniferous tubules is supported by the fact that the symptoms still persist in December (in some bulls even as late as February), although winter-time is climatically congenial for normal functioning of the testes. The summer degeneration of the semeniferous tubules is accompanied by a contraction in diameter from 250μ to 190μ.

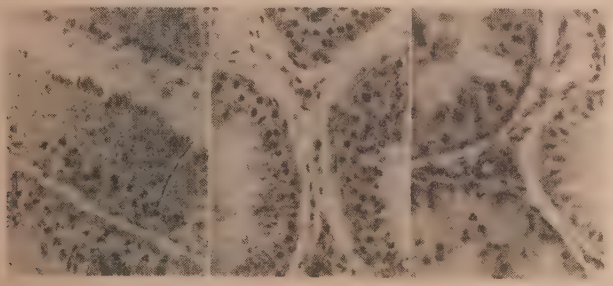

Figure 5 Figure 6 Figure 7

BULL — Cross Sections: 5) tubule at peak of activity 6) tubule during summer inactivity 7) tubule in late summer showing symptoms of vitamin deficiency

The seasonal changes in spermatogenesis of the Arabian bull are not along defined lines, but may be classified as follows: (a) full activity (March-May), (b) depression of activity and appearance of summer-sterility symptoms (June-August), (c) futrher atrophy attributable to deficiency of vitamin A (July-November), (d) partial regeneration of some tubules side-by-side with persisting symptoms of avitaminosis A (December-February).

RAM

The Awassi ram has become thoroughly acclimatized in the course of centuries. Outwardly, it is characterised by the conspicuous development of its fat-tail. The scrotum is moderately covered with woolly hair. The tupping season takes place during a short period of long hot days about the end of June and the beginning of July, although he usually remains sexually active and fertile till August, while in some individual ewes there may be a recurrence of heat in late summer and autumn. In this respect the Awassi differs markedly from rams of other breeds, which are thought to be fertile only during the short days around the winter-solstice, while exhibiting symptoms of summer sterility at the time of long photoperiods.

In the Awassi ram an increase in the activity of the semeniferous tubules can be observed from June to August, whereas in April the activity is almost nil and the microscopic sections show signs of atrophy and general disorganization in the semeniferous tissue. In September — some two-three months after the peak of activity — symptoms of summer sterility can be detected, similar to those described in reference to the camel and the bull. Surprisingly enough, a similar condition frequently persists well into December, although at that time the temperature is very congenial.

BUCK

The principal domain of goats in Israel is in the hilly region, where natural pasture is more abundant and mean temperature in spring and summer lower than in the coastal plain.

The native buck normally mates in July and August, while parturition takes place in December-January. Like the native bull and the ram, the buck is also capable of service all the year round, but it is doubtful whether unseasonal mating ever results in conception.

As opposed to the other animals described, no atrophy of the semeniferous tubules has been observed and it may be presumed that the buck remains sexually active throughout the year. However, the doe, even under conditions of up-to-date management, maintains the seasonal polyoestrous character of the sexual cycle.

DISCUSSION

The seasonal changes occuring in the semeniferous tubules of some indigenous races of farm animals — camel, bull, ram and buck — have been histologically examined. It has been established that, with the exception of the native buck, a phase of active production of spermatozoa alternates in these animals with a period of "summer-steriity".

In the bull and, to some extent, in the ram, degeneration symptoms have been observed which cannot be entirely accounted for the factors of temperature and length of day and it is suggested that they are produced by a deficiency of vitamin A in the dry plants on which the animals feed for 7—8 months in the year. Whereas the camel and the buck live on foliage and the soft parts of thorny plants, thus finding a plentiful supply of fresh succulent feed during most of the year, cattle and sheep find a sufficient supply of green fodder only in the winter pasture. The atrophy of semeniferous tubules observable in the camel is apparently caused by high summer temperature: the structure of the scrotum and the proximity of the testes to the body support this assumption. In the bull, the process of disintegration of the tubules apparently comes about in response to changes in temperature and length of day, while avitaminosis A probably contributes to the continuation of the process in the summer. In this connection it is noteworthy that no regeneration occurs during the cool winter months until the pasture has reached a condition in which it can satisfy the requirements of cattle and sheep for green fodder. The histological development in the ram resembles roughly that obtaining in the bull, but the period of full sexual potency occurs later, during the hot months of June and July.

The uninterrupted activity of the semeniferous tubules in the buck, in addition to the vitamin-rich food, may be accounted for by the lower temperatures prevailing in the mountainous region, to which goat-keeping in Israel is mostly confined.

It appears that improved care and feeding have not materially altered the breeding habits of the indigenous farm animals. The periodicity of the sexual behaviour should therefore be regarded as a predominantly hereditary trait which must be taken into consideration when crossing with foreign breeds is contemplated.

The fact that the sexual cycle in pure-bred cattle also shows traces of seasonal fluctuation, seems to indicate that the solution to problems of defective fertility lies in the selection of breeds and individuals sexually adjusted to the enviromnent rather than in management and therapeutic methods.

Some explanation of the seasonal interruption in sexual activity may perhaps be found in the function of the thyroid gland. A survey of thyroid activity carried out on the animals used for the histological observations[7] suggests that the peak of sexual activity as denoted by the state of the semeniferous tubules, coincides with intensive absorption of thyroxyne, whereas the degeneration period is indicated by cessation of thyroid activity or accumulation of colloid within the gland lumen.

REFERENCES

1. Marshall, F. H. A., 1937, *Proc. Royal Soc.*, 122 413.
2. Bonsma, J. C. *et al.*, 1940, *Union of S. Africa Dept. Agric. Bul.*, 223.
3. Phillips, R. W., 1948, First World Congress for Artificial Insemination, Milano.
4. Bogart, R. and Mayer, T. D., 1946, *Mo. Agr. Exp. Sta. Res. Bul.*, 402.
5. Schindler, H., 1952, The Hebrew University of Jerusalem.
6. Erb, R. F. *et al.*, 1947, *J. Dairy Sci.*, 30, 687.
7. Volcani, R., 1952, The Hebrew University of Jerusalem.

AEDES AEGYPTI AS A VECTOR OF WEST NILE VIRUS

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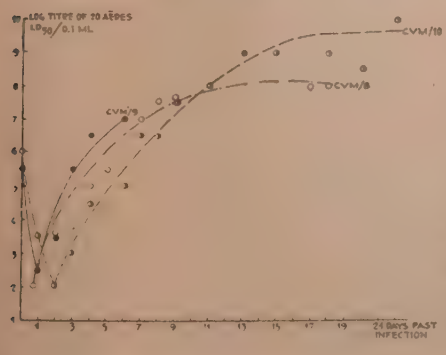
A virus, apparently identical with the West Nile virus, has been isolated from patients during a number epidemics in Israel[2,3]. Epidemiologically and experimentally, *Culex molestus*, appears to be a vector[5,3] and it has also been demonstrated that another mosquito, *Aedes aegypti*, is capable of transmitting the virus to laboratory animals[4]. Further evidence is now presented that multiplication of the virus occurs within the body of this mosquito and thus transmission of the disease is not merely a mechanical act.

1. A group of *Aedes*, six days after emergence, were starved for 24 hours and then fed on a suspension of mouse brain passage of the virus (strain EV 101/M8) mixed with honey and defibrinated blood. This initial meal contained 10^4 mouse LD_{50} doses per 0.1 ml. The infected mosquitoes were kept at 28°C at a relative humidity of 65—70% on a diet of honey and water and after one week, those still alive were removed and counted. They were then killed by freezing, emulsified in 10% serum saline and well mixed with honey and defibrinated blood. A second group of mosquitoes was then fed on this mixture and the procedure was repeated for a total of five passages. A group of mosquitoes of the 5th passage was emulsified and injected, at a dilution of 1:10, intraperitoneally into 6 mice aged 14 days. Of these mice 5 died with characteristic signs of West Nile diseases, indicating the presence of virus in the mosquitoes. It is calculated that the final dilution of the original meal was 7×10^{-9}, and as the initial titre was 10^4 mouse LD_{50} doses per 0.1ml, multiplication must have occurred within the bodies of the mosquitoes. This technique is a modification of that first described by Professor S. Adler for phlebotomus[1].

2. Large batches of *Aedes aegypti*, 7-8 days after emergence, were infected with three different lines of West Nile Virus. One batch (CVM/8) was infected by the technique previously described[4] on embryonated eggs inoculated with a strain (P.H.106 M4) recently isolated by Dr. N. Goldblum. Two other batches were infected on hamsters which had been inoculated in one case (CVM/9) with an egg adapted line of virus (EV101/E12) and in the other case (CVM/10) with a hamster adapted line (EV101/OHA/11). The hamsters were bled and the titre of virus in the blood at the time of feeding was determined by intraperitoneal injection in young mice and this was confirmed by the titration of emulsion of a group of mosquitoes immediately after feeding. At successive intervals thereafter, groups of 20 infected mosquitoes were removed, emulsified, and their virus content determined. From the graph it can be seen that at least in the series CVM/9 and 10, there occurred an initial rapid fall of the titre of virus in the mosquitoes, followed by a rise after 1-2 days which surpassed the initial titre within a week and continued to be significantly greater than the amount ingested.



3. Examination of groups of infected mosquitoes revealed the presence of virus in the head, thorax, abdomen, wings and legs, indicating distribution, if not development, in all portions of the body, a condition not associated with mechanical transmission of a virus.

This evidence, taken together with the fact of transmission of the disease by *Aedes aegypti* in the

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laboratory, indicates that this mosquito is capable of behaving as a true, biological vector of West Nile virus.

Thanks are due to Mrs. E. Krauthamer for technical assistance and to Dr. N. Goldblum for his gift of a strain of the virus.

REFERENCES

1. Adler, S., 1928, *Trans. Roy. Soc. Trop. Med. Hyg.*, **22**, 177.
2. Bernkopf, H. and Levene, S., 1952, *Bull. Res. Counc. of Israel*, **2**, 209.
3. Goldblum, N., 1952, Personal communication.
4. Goldwasser, R. A. and Davies, A. M., 1953, *Trans. Roy. Soc. Trop. Med. Hyg.*, **47** 336
5. Olejnik, E., 1952, *Bull. Res. Counc. of Israel*, **2**, 210.

NUTRITIVE AND BAKING PROPERTIES OF CAROB GERM FLOUR

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INTRODUCTION

Carob seeds are used in Cyprus and Israel as a source of gelatinizing and tanning agents. The separation of the coat and skin from the endosperm by mineral acids produces a by-product "embryo flour", which is rich in nutrients, particularly protein. The flour might be used to increase the nutritive value of baked products or to produce high protein foods for diabetics.

PROPERTIES AND COMPOSITION OF CAROB EMBRYO FLOUR

Carob embryo flour is odorless, tasteless and yellow-green in colour. The green tinge is especially apparent after wetting with water. After boiling in water, it acquires a leguminous taste. When improperly prepared, the flour may contain black particles which are fragments of the burnt seed cover.

The average composition of nine samples was: protein ($N \times 6.25$) — 54.3%, Nifex — 25.1 %, ash—5.2%, fat—4.8%, crude fibre -1.4%, moisture –9.2%.

Carob embryo flour which contained 56.0% total proteins as calculated from the nitrogen content was found to contain 53.8% true proteins as determined by the cupric hydroxide method of Stutzer. The digestible proteins of this sample as determined by the Wedemeyer modification of the pepsin-hydrochloric acid method[2] were 52.2%, giving a protein digestibility of 93%. These results agree with those of Kling[3].

In order to compare the proteins of carob embryo flour with other proteins, they were separated into groups with the aid of various solvents. Although the method did not yield pure protein goups, it gave an adequate separation for the purpose of comparison. The total protein was separated into the groups shown in Table I. The differences between the leguminous proteins and cereal proteins are quite outstanding. The alcohol soluble proteins are of a relatively smaller percentage when compared with cereal proteins such as those of wheat, rye, etc.

TABLE I

Group	Basis: 100g embryo flour (%)	Basis: 100g embryo flour protein (%)
Albumins (water soluble)	8.1	14.5
Globulins (5% K_2SO_4 soluble)	28.0	50.0
Prolamins (70% alcohol soluble)	1.9	3.4
Gluteline and others (by difference)	18.0	32.1

The percentages of the different carbohydrates found in carob embryo flour were as follows: reducing sugars—1.4%, sucrose—2.8%, dextrins—3.3%, pentosans—4.2%.

The 5.2% of total mineral matter included 2.67% phosphorous (calcd. as P_2O_5) and 0.7% calcium (calcd. as CaO).

NUTRITIVE VALUE OF CAROB EMBRYO FLOUR PROTEINS

The nutritive value of carob embryo flour proteins was assessed by the following three methods.

Nitrogen balance method

The biological value of carob embryo flour protein was determined using the well known method of Mitchell. Nine adult male rats were used. The test diet was prepared by incorporating carob embryo flour in a protein-free but otherwise adequate basal diet to give a final protein level of 9 g per 100 g ration.

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The protein digestibility was found to be 89% and the biological value 59. Thus the nutritional value of carob embryo flour protein as determined by this method is inferior to that of most animal proteins.

Regeneration of liver protein in protein depleted rats

Thirty-three rats were used for the test as described by Guggenheim and Buchler-Czaczkes[4]. The mean daily increase of liver nitrogen was found to be 2.25 mg N/g liver as compared with dehydrated egg—2.33, meat—2.17, casein—2.43, processed soya flour—2.60, peanut meal—1.63, maize flour—1.07, wheat flour (white)—0.53, gelatine—1.20 and fish meal—1.16.

Regeneration of haemoglobin in protein-depleted rats

Eleven rats weighing 150—250 g were tested according to the method described by Buechler and Guggenheim[1]. After 20 days on 9% carob embryo flour protein diet, the haemoglobin level of the blood rose on the average by 1.6 per 100 g. Other food proteins tested in the same way induced the following increases in haemoglobin concentration (in g/100 g blood): dehydrated egg—2.4, meat—2.2, casein—1.5, processed soya flour—2.0, peanut meal—1.3, maize flour—1.3, wheat flour (white)—0.4, gelatine—0.5.

USE OF CAROB EMBRYO FLOUR IN BAKING

The proteolytic activities of wheat flour and mixed flour were determined by the Swanson-Tague method over a period of three hours. Wheat flour gave 0.71 mg N as free amino acids, and a mixture of wheat flour and carob-embryo flour containing 10% of the latter gave 0.62 mg N as free amino acids. From these results, it can be seen that the addition of 10% carob embryo flour does not affect the activity of the proteolytic enzymes of wheat flour.

The diastatic activity of wheat flour and a mixture of wheat flour and carob embryo flour containing 10% of the latter was determined by the Kent-Jones method. Wheat flour gave 0.93% maltose, and the mixed flour 0.87% maltose. These results indicate that the addition of 10% carob embryo flour to wheat flour does not increase the diastatic activity.

The addition of carob-embryo flour to wheat flour did not increase the amount of gluten when washed in the usual way.

The effect of the addition of 10% carob-embryo flour to wheat flour on gas production and retention was investigated by the volumetric method. The dough was prepared from 100 g flour containing 10% mixture, 60 ml of water, and 3 g bakers' compressed yeast. The fermentation time was 5 hrs at a temperature of 30°C. The volume of gas produced was measured half hourly. The results of this experiment are shown in Figure 1.

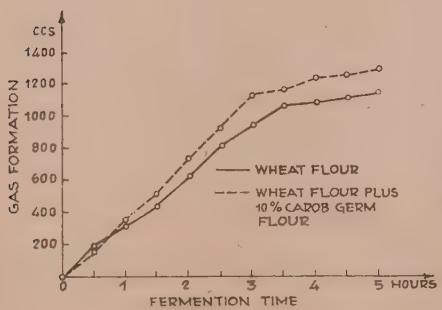

Figure 1

The volume of dough produced from wheat flour after fermentation was greater than that produced from the same quantity of the mixed flour; from which fact it was concluded that the addition of carob-embryo flour to wheat flour would cause a decrease in the bread volume. The amount of carbon dioxide produced was higher in the mixed flour. This effect may be ascribed to the provision of a more favourable nutrient medium for the growth and development of the yeast cells by the proteins and salts of the carob embryo flour, and also the differing acid condition of the dough produced from mixed flour.

In order to produce bread with high protein content, amounts of carob embryo flour ranging from 1 to 10% were added to wheat flour, and the mixture was baked according to the A.A.C.C. method.

With small additions (1—3%) of carob embryo flour, the bread was yellowish, its taste was normal, and there was a slight increase in its acidity. With larger additions, there was a negative effect on the properties of the dough. The addition of 5% carob embryo flour to wheat flour used in baking biscuits resulted in a slight decrease in the volume of the biscuits. Their taste was not affected, but the crust was browner, and the biscuit interior was darker. Bread rusks and biscuits for diabetics may be pre-

pared from a mixture of 70% carob embryo flour and 30% wheat flour of good baking quality. The baked products were found to contain 20—25% carbohydrates and 42—43% proteins, calculated on an air dry basis. In the preparation of bread for diabetics, it was found necessary to incorporate into the dough 0.5% sodium bicarbonate, calculated on the flour basis.

TABLE II

Volume of breads prepared from 100 g flour (whear flour + carob embryo flour)

Volume (cm^3)	Carob embryo flour added to wheat flour (%)
406	0
401	2
390	3
368	5
350	10

Figure 2

Baking tests with addition of carob germ flour. *Left to right:* 70% (diabetics), 10%, 5%, 0%.

The sponge method of baking was found to be more suitable than the straight method. 100 kg flour containing 13% moisture yielded 160 kg bread. The high yield was due to the high water absorption of the carob-embryo flour. Rusks were also prepared by the same method except for the addition of eggs.

REFERENCES

1. Buechler, E. and Guggenheim, K., 1949, *Blood*, **4**, 964.
2. Schwarzmann, M., 1933, The Carob Tree, *Bull.* 1, Dept. of Agriculture and Forestry, Government of Palestine.
3. Kling, M., 1928, *Die Handelsfuttermittel*, Ulmer, Ludwigsburg.
4. Guggenheim, K. and Buechler-Czaczkes, 1950, *Brit. J. of Nutrition*, **4**, 161.
5. Wedemayer, K., 1935, *vide* Boehmer, Juckenack and Tillmanns, 1935, *Handbuch der Lebensmittelchemie II*, Springer, Berlin, 611.

DISHARMONIC FAULTING, A TECTONIC CONCEPT*

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At the close of the Lower Tertiary mountain building in the Levant in late Oligocene or proto-Miocene, large depressions were formed. The trends are either Northeast or Northwest with a remarkable absence of North-South alignments. These depressions which surround the Arabian Shield (Red Sea Graben, Mediterranean coastal embayments, Mesopotamian trough, Syrian and Galilean Intermountain basins) were subsequently filled with marine, brackish and continental deposits in the Neogene. In the late Pliocene or proto-Pleistocene a separate set of depressions came into existence, the meridional "chain of troughs" Akaba-Gulf, Wadi Araba, Dead Sea, Jordan Valley. This composite rift-valley with an average width of 10 km dissects with its border faults the major and minor Tertiary folds of predominantly Northeastern directions (see structual pattern-map by Picard)[1].

Leopold von Buch[2] noted the discrepancy in formation and topographic feature between the opposite escarpments of the Dead Sea, but it was Lartet[3], however, who emphasized the unilateral character of this trough. Following Lartet's[3], Fraas'[4] and Blanckenhorn's[5] observations, Suess[6] in his masterly manner finally synthesized their observations in the "Antlitz der Erde":

"Die Jordanlinie ist ein Bruch, aber waehrend im Osten dieser Bruch an einer einzigen grossen Hauptspalte sich vollzog, entstanden im Westen mehrere, parallele — Brueche, auf welchem der Westfluegel nicht im ganzen Koerper, sondern in Treppen absank, sodass ein einseitiger Graben entstand."

Geological maps [3,5,7,8,9,10,11] as well as the writer's map clearly reveal the structural contrast of both graben "lips" of the Southern Wadi Araba. Here, the western border zone is dissected by numerous faults of small size and relatively small throw, occassionally curved and arranged en échelon. The mountains of the eastern border, on the other hand, are split by two large regional faults of many hundred kilometres length extending from the Hedjaz to the area of Petra and probably up to the Dead Sea. In the southern Wadi Araba Rift the regional faults are thus attached to the crystalline basement rocks while the small-sized fault pattern opposite occurs prevalently in sediments. Rectilinear faults of small dimensions producing miniature Graben and — Horsts are found in the Southwest corner of the Akaba Gulf region (Israel-Egypt boundary) where sedimentary and crystalline rocks frequently alternate.

The western rim of the Northern Wadi Araba is nearly free of visible faults. The Cretaceous and Eocene folded sediments plunge into a depression which is, moreover, filled up by Cenozoic inland deposits. It is in effect difficult to define here a graben-border. Any marginal faults are thus concealed below the sedimentary cover. Not so on the eastern side of the valley where Nubian sandstone of great thickness or crystalline basement rocks are exposed. Although a detailed survey is missing, it is quite evident that the eastern slopes of the Northern Wadi Araba graben are likewise bordered by meridional faults of regional extent. However, in the Petra and Tafileh area diagonal fractures cross the mountains, causing downthrow and down-slipping of Upper Cretaceous sediments. It is in this area of small block-faulting that — characteristically enough — the clear picture of a well-expressed marginal major fault is again destroyed.

The southwestern part of the Dead Sea Graben was recently (1947) surveyed by J. Vroman on behalf of the Jordan Exploration Company. Based on his co-workers, observations the author came to the following conclusions**:

"While very little faulting, mostly parallel to the Northeastern folds, occurs in the Judean Desert, a very intricate net of fault lines appears below sea level at the Western side of the Dead Sea Graben. The faults cut both the Tertiary major and minor folds. The fault-planes are vertical or more often dip slightly to the East. They run parallel with the trend of the graben and curve away from this direction

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in a crescent-shaped manner. They average a few kilometres in length and never continue for more than ten kilometres.

The average maximum throw of the curved faults is between 100 and 200 metres. Two faults, however, show a bigger throw of several hundred metres. These are the zig-zag step faults bordering the mountains west of the Massada Plain. In contrast to the usual textbook conception no single main fault cutting the whole area and defining the main graben-border was found. It is nevertheless possible that step-faults of small extension but of larger throw may reach down to the depths of the basement and form here a fracture equal in regional magnitude to the exposed faults of the crystalline southernmost Transjordan. Such a difference of faulting between super- and substructure has been designated by us as *disharmonic faulting*. (Term first proposed in our publication on the Andes[12])".

A gravity survey carried out for the same company indicated according to Prof. Nettleton's interpretation a fill of 7000 metres in the graben centre. If we add to this figure 1000 and more metres for the heights of the surrounding mountains, the dimensions of this 18-kilometre-wide graben become comparable with oceanic deep sea troughs. In this case, the throw of our postulated basement fault may attain many thousands of metres, as outlined in Figure 1.

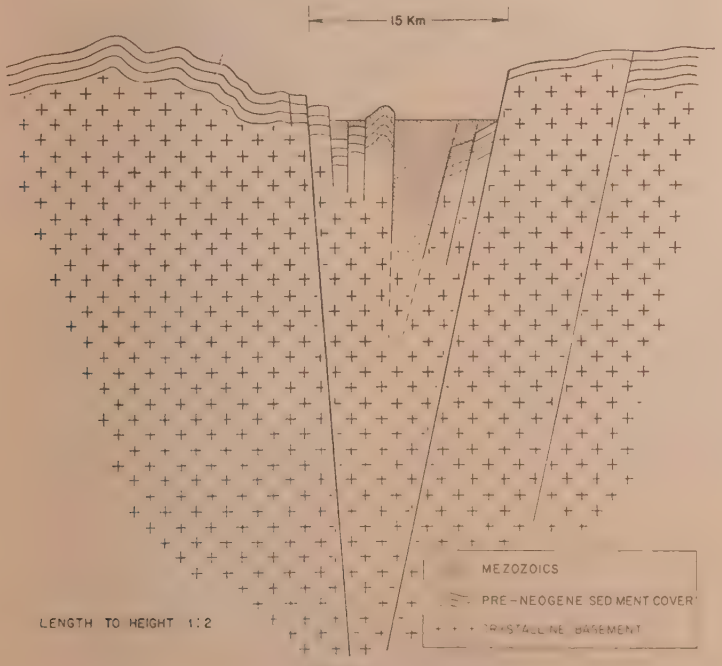
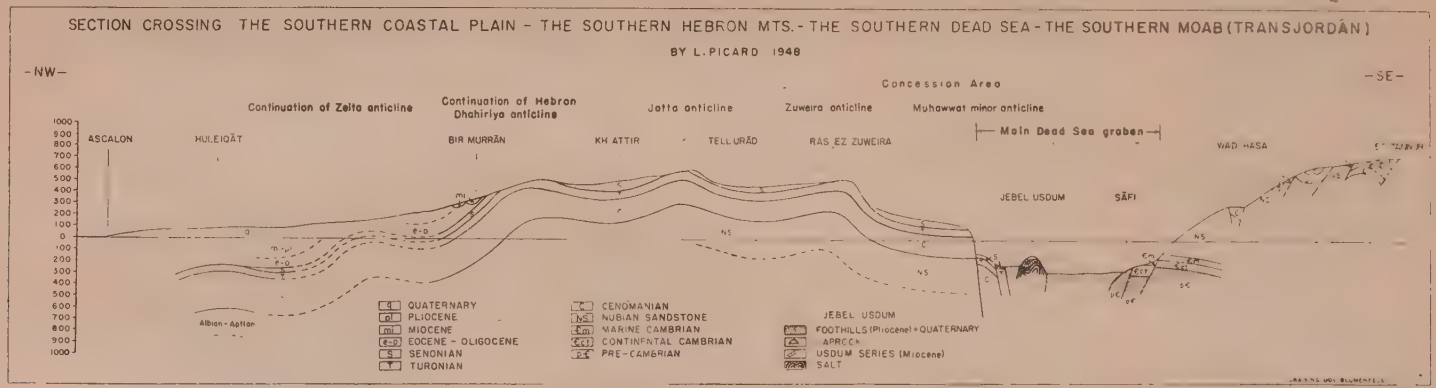


Figure 1

The tectonic pattern of the northern part of the Dead Sea Graben and its continuation to the north of Jericho has been described by the writer in 1931[13,14]. Crescent-shaped block-faults of considerable throw form the major cliffs at the sea and at the edge of the Jordan Valley. Yet no principal regional border fault could be located. Such a major marginal fault, however, must exist at the Transjordan side of the Dead Sea coinciding with the greatest topographic depth of the sea immediately adjacent to the eastern shore. Nevertheless diagonal shear faults divide the region in "wedgelike blocks". Such downfaulting obscures the continuity of the border-fault as for instance in the ridges east of the Lisan peninsula.

Referring to our former discussion on the Northern Jordan Graben[15] (p. 79–84) two major points should be emphasized:



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1) Between Wadi Fari'a and Beisan, the Jordan depression narrows so considerably that it creates the impression of being dissected only by one main fault, not forming a graben.

2) From Beisan to the Huleh depression the country is dissected into numerous tilted blocks. Their faults enter the graben in crescent form and are replaced by other curved faults. Thus the Western Graben flank is again free of a distinct border fault. In view of the perfect morphological aspect of the graben, rectilinear and meridional faults of regional extension have to be searched for underneath the cover which consists here predominantly of Eocene and Neogene sediments. Moreover, evidence of deep-seated fractures, parallel with the trend of the graben is found in the 12-km-long basalt dyke-ridge which crosses the Neogene south of Tiberias in a perfect North-South direction at the edge of the graben. This Pleistocene basalt fissure must finally be considered an indication of the tensional origin of the graben. (A similar though smaller North-South basalt dyke-ridge is known from the northwestern border of the Huleh depression.)

Disharmonic faulting thus becomes a fundamental concept in tafrogenic tectonics. Associated with it are faults curved and shaped en échelon. They are found in downthrown or down-warped portions of the graben where torsion-movements in the sedimentary cover have produced crescentic and rotational faults. (Incidentally, they were the crescentic faults of Mount Gilboa and Mount Carmel, on which Bailey Willis [16,17] had based his compressional ramp theory). Busk[18], was the first to describe this fault-pattern from the Suez Rift Valley in his illuminating *Earth flextures*. Other examples can be followed up in East Africa,[17] in the Andes [12]in the North American Basin ranges, etc. New examples from the latter region were most recently described by Pardee[19].

REFERENCES

1. Picard, L., 1953 The Structural Pattern of Israel, *Bull. Res. Counc. of Israel*, in press.
2. Buch, L. von, Appendix in Robinson, E., 1841, *Biblical Researches in Palestine*, London 2.
3. Lartet, L., 1869, Essai sur la Géologie de la Palestine, *Ann. Sci. Geol.*, Paris, 1.
4. Fraas, O., 1867. *Aus dem Orient* I, Stuttgart.
5. Blanckenhorn, M., 1912, *Naturwissenschaftliche Studien am Toten Meer und Jordantal*, Berlin.
6. Suess, E., 1908, *Das Antlitz der Erde*, 3rd ed. 1, 481.
7. Dubertret, L., 1942, *Carte Geologique du Moyen Orient*, 1:2,000.000.
8. Hull, E., 1886, Memoirs on the Geology and Geography of Palestine, *Palestine Exploration Fund*, London
9. Kober, L., 1919, Das noerdliche Hegaz, *Deutsche Akad. Wiss. mat — nat. Kl.*, Wien, 91.
10. Blake, G. S. (in Ionides and Blake), 1939, *The Water Resources of Transjordan*, Crown Agent, London.
11. Shaw, S. N., 1947, *Geological Map of Southern Palestine*, Jerusalem, Govt. Press.
12. Picard, L., 1948, La structure du Nord-Ouest de l'Argentine, *Bull. Soci Geol. France*, 5 ser., 18, 822.
13. Picard, L., 1931, *Geological Researches in the Judean Desert*, Jerusalem.
14. Picard, L., 1931, Grabenstructuren im Jordantal, *Deeke Festschrift*, Berlin.
15. Picard, L., 1943, Structure and Evolution of Palestine ,*Bull. Geol. Dept. Hebrew Univ.*, Jerusalem, 4.
16. Willis, B., 1928, Dead Sea Problem: Rift Valley or Ramp Valley, *Bull. Geol. Soc. of America*, 39, 490.
17. Willis, B. and Picard, L., 1932, The Jordan Valley and Judean Highland, *Geol. Mag.*, 69, 97.
18. Busk, G. H., 1929, Earth Flextures, *Geol. Series*, Cambridge.
19. Pardee, J. T., 1950, Late Cenozoic block-faulting in Western Montana, *Bull. Geol. Soc. of America*, 61, 359.

THE GERMINATION OF LETTUCE SEED
III. THE EFFECT OF LIGHT ON GERMINATION*

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I. INTRODUCTION

The main points investigated in this paper were (1) the effect of radiation of different wave lengths on the germination of lettuce seeds, (2) the effect on germinating seeds of different periods of irradiation following different time intervals after inception of imbibition, (3) the validity of the product law (quantity of stimulus law) in relation to photoblastism.

II. METHODS

The germination methods employed followed the procedure previously described by Evenari[1]. Seeds of the varieties Grand Rapids and Progress used in these experiments were kindly supplied by the Ferry Morse Seed Co., San Francisco. All experiments were carried out with seeds from the same batch.

About 100 seeds were placed on filter paper in Petri dishes and soaked in 3cc distilled water. The seed dishes were irradiated in a dark room for the required length of time, whereupon they were placed in a tin box and returned to the incubator which was set at 26°C. Illumination for all dark-room work was secured with the aid of a blue Corning glass filter No. 430, proven neutral in regard to germination for the durations of application employed. All germination percentages were determined after 48 hrs. Four Petri dishes were used for each treatment, while in some doubtful cases as many as ten replications were employed. Each experiment was repeated at least twice.

The light intensities were measured with a Norwood Exposure Meter calibrated in foot candles (F.C.). When white light was used, it was normally applied at 250 F.C. When a filter was employed, it was interposed between the lamp and the seeds.

When decoated seeds were required, the fruit and seed coats were removed prior to germination by rubbing between fingers[2], thus opening up and partially removing the endosperm.

III. THE INFLUENCE OF DIFFERENT WAVE LENGTHS

The effect of different filters

Wratten and Corning filters were used, since no spectrograph was at our disposal. As Flint[3], and Flint and McAllister[4,5] had extensively dealt with the action spectrum of germination of lettuce seed, the present investigation was largely concerned with finding filters which would respectively prove most effective for stimulating and inhibiting germination.

For the comparative study of the effect of different filters, the irradiation period was adjusted for each filter according to its total transmission, so that the amount of light energy transmitted should be the same. All the experiments were carried out at 26°C. As indicated by the results in Table I, some filters produced a stimulating effect on germination, others resulted in inhibition, while a number of filters had no effect at all.

The germination index *G.I.* represents the ratio of the germination percentage of irradiated seeds to that of control seeds kept in darkness. The symbol *G.I.*(*R*) has been introduced to signify the ratio of the germination percentage resulting from irradiation through a given filter, following irradiation through a red filter (Corning glass No. 245) to the germination percentage obtained by control application of the red filter alone. Strongest inhibition was produced by Wratten infrared filter 88A.

In view of the inhibiting effect of infrared radiation, it was considered necessary to ascertain the

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transmission of the blue and green filters in the infrared region. The results obtained with the use of a Beckman spectrophotometer are given in Table II.

It can be readily seen that those green and blue filters which give high transmission in the infrared (Nos. 54, 62), exerted a very strong inhibiting effect on germination while those filters whose infrared transmission is low or nil, had a very insignificant or no effect on the germination percentages (Nos. 58, 60, 61). It follows that in the case of the green and the blue filters, it was not the transmission in the visible region that caused inhibition, but the transmission in the infrared. To test this conclusion further, an additional experiment was performed in which infrared radiation was filtered out by means of the following solution: 10 g $Cu(NO_3)_2$, 1 cc HNO_3, 89 cc H_2O (dist.)[6]. The transmission of this solution is 98% at 400 mμ, 98% at 450 mμ, 96.5% at 500 mμ, 81% at 550 mμ, 42% at 600 mμ, 6% at 650 mμ and 0% at 700, 750 and 800 mμ.

Germination percentages obtained with combinations of blue filters and solution (with or without pre-treatment with red), are given in Tables III and IV.

The results obtained prove conclusively that the blue and green filters produce inhibition of germination solely on account of their transmission in the infrared. This fact seems to have been overlooked by other authors[3,4,7,8] in their work on lettuce and other photoblastic seeds.

We would suggest an analogy between the stimulating effect of the yellow region and the seemingly inhibiting effect of the blue and green. The yellow probably derives its stimulating effect from its transmission of red radiation.

Behaviour of decoated seeds in relation to infrared radiation

It was shown in an earlier paper[2] that the same high germination percentages were obtained with decoated seeds kept in darkness as with untreated seeds subjected to white light. Here, the effect of infrared radiation on the germination of decoated seeds was investigated.

The results in Table V show that infrared has no inhibiting effect on the germination of decoated seeds.

The effect of temperature on the response to inhibiting radiation

Seeds of the variety Progress have proved to be non-photoblastic at 26°C, since at that temperature their germination was not affected by irradiation through infrared-transmitting filters (Table VI).

The results of a supplementary experiment, carried out at 29°C, show, however, that at the higher temperature the photoblastic response is very pronounced. Irradiation through filter No. 47 completely arrested germination at 29°C, while the dark control germinated to the extent of 27 per cent.

In the variety Grand Rapids, photoblastic effects are also conditioned by temperature. At 20°C, no inhibiting effect was obtained with the use of filter No. 47 (Table VII).

Effect of time on the reversibility of stimulation

An experiment was designed to determine the effect on germination of the time interval between stimulating irradiation and the subsequent application of inhibiting radiation. Different lots of Grand Rapid seeds which had been soaked for 2 hours and then irradiated for 30 seconds through a red filter, were subsequently subjected to 4 minutes of inhibiting radiation directly, and after 6, 8 and 10 hours, respectively.

The results given in Table VIII show that the effect of the inhibiting radiation diminishes as the time interval between the application of stimulation and inhibiting radiation is lengthened. After the lapse of 10 hours, the stimulation produced by red light cannot be reversed to any appreciable extent.

IV. DEVELOPMENT OF PHOTOSENSITIVITY OF GERMINATING LETTUCE SEEDS IN THE COURSE OF IMBIBITION

In order to follow the changes in photosensitivity during the imbibition period, several lots of seeds were germinated. One lot was set aside as dark control, while other lots were irradiated for 2 minutes with 250 F.C., each after a different time interval from the inception of imbibition (Figure 1). It can be seen that photosensitivity sets in after 6 minutes of soaking, and it becomes pronounced after 8 minutes. Maximum germination percentage is attained after 16 minutes and after 20–30 minutes, at 22°C and 26°C, respectively.

In view of the fact that the quantity of light employed here was in excess of requirement, a similar series of experiments was carried out which involved the application of much shorter irradiation periods (5, 10, 30, 60 sec.) after longer time intervals (Figure 2). This series did not include records between the 8th and 24th hour. There was a steady increase in photosensitivity during the first 8 hours of imbibition. It is also obvious that by the 24th hour of soaking, photosensitivity is already in an advanced state of decline

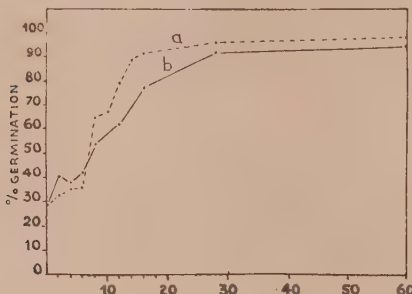

Figure 1

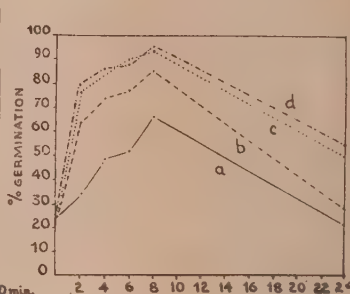

Figure 2

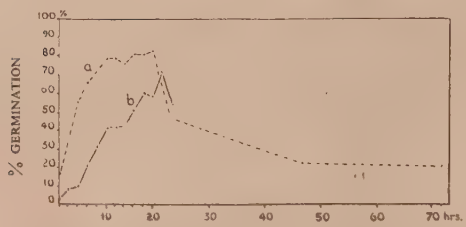

Figure 3

Figure 1. — *The effect on germination of irradiation for 2 minutes applied at different stages of imbibition, at two different temperatures.*
Germination percentages at 22°C (a) at 26°C (b) plotted against time intervals from inception of imbibition.

Figure 2. — *The effect on germination of irradiation of varying duration applied at different stages of imbibition.*
Germination percentages obtained with 5 seconds (a) 10 seconds (b) 30 seconds (c) 60 seconds (d) of irradiation plotted against time intervals from inception of imbibition.

Figure 3. — *The effect on germination of irradiation for 5 seconds applied at different stages of imbibition, at two different temperatures.*
Germination percentages at 26°C (a) at 28°C (b) plotted against time intervals from inception of imbibition.

Figure 3 shows the results of an experiment in which the irradiation period was 5 seconds, one set being carried out at 26°C and another 28°C. It was seen that at 26°, maximum photosensitivity was reached after 8 hours and was maintained till about the 20th hour, when a rather rapid decrease set in. This roughly coincided with the stage at which the first visible signs of germination could be discerned. At 28°C, the maximum was reached only after 20 to 22 hours.

With a view to assessing the photosensitivity after relatively long periods of imbibition, an experiment was carried out with two lots of seeds which were allowed to soak for 48 and 72 hours respectively. Those seeds which had already germinated were removed into darkness, while the remainder were subjected without delay to irradiation with white light for different periods (Table IX).

It can be seen that even after 72 hours of soaking in the dark, the seeds still retain some photosensitivity, even though considerably reduced.

Figure 4 follows the progress of photosensitivity to stimulating and to inhibiting radiation. In seeds receiving stimulating radiation for 30 seconds through Corning Glass Filter No. 245 (curve a), photo-

G.I.

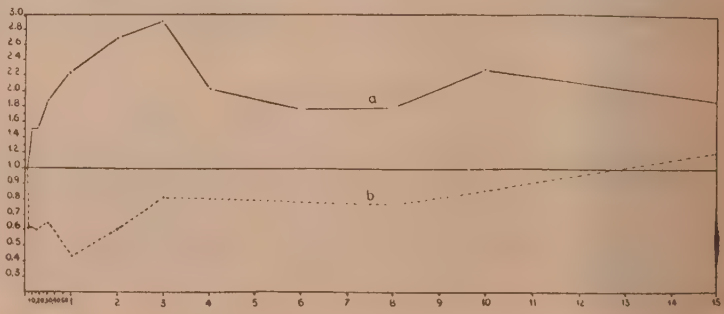

Figure 4. — *The effect on germination of stimulating and inhibiting radiation.*
Rates of germination, expressed in terms of *G.I.*, plotted against time intlervas from inception of imbibition (min. and hrs.). The curve of stimulation (a) was obtained by irradiation for 30 sec. through Corning glass filter No. 245; the curve of inhibition (b) by irradiation for 4 min. through Wratten filter No. 47.

sensitivity could already be discerned after 4 to 10 minutes of soaking, and it attained its peak at the end of 3 hours, *i.e.*, at a much earlier stage of imbition than in the case of white light. The inhibition of germination resulting from irradiation through Wratten filter No. 47 for 4 minutes (curve b), reached a maximum as early as one hour after the start of imbibition, whereupon it declined sharply.

Figure 5 which represents rate of water intake by the seed, shows in how far photosensitivity is a function of imbibition.

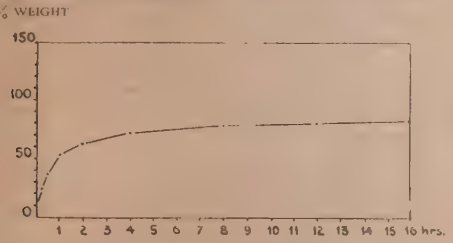

Figure 5. — *Relation between the duration of imbibition and the water intake of seeds.*
The weight of imbibed water, expressed as percentages of the weight of dry seeds, plotted against time intervals from inception of imbibition (hours).

III. THE PRODUCT LAW

As previously pointed out[3,8], the product law appears to be operative in the case of photoblastism of different seeds. The law stipulates that the germination percentage is not affected as long as the product *light intensity* × *irradiation period* remains constant, without regard to changes in the values of the component factors. The validity of the product law in relation to photoblastism of lettuce seeds was tested in relation to white, stimulating, and inhibiting light.

The results obtained with the use of white light in three sets of experiments are given in Table X. It appears that, in the case of lettuce seeds, the product law is valid for the higher product values associated with high germination percentages. On the other hand, it appears to be completely inapplicable to the lower product values.

With stimulating radiation (Corning glass filter No. 245) the product law appears to be valid for the whole range of the light intensity × time products employed (Table XI). Its validity is also borne out by the results obtained in analogous experiments with inhibiting light (Wratten filter No. 47), following application of stimulating light (Table XII).

VI. DISCUSSION

It is still too early to fit the findings relating to the photoblastic behaviour of lettuce seed into a general theory of photoblastism. It is felt, however, that an attempt to sort out the maze of known facts into some acceptable scheme is now opportune. Even though, at this stage, such an attempt may involve a certain amount of conjectural reasoning, it is hoped that it will ultimately crystallize into a working hypothesis which can then be put to the test of additional experiments.

It seems that some of the facts brought out in this paper may be of help in solving the problem of localization of the light effect.

It is known that the process of swelling in the lettuce seed is completed only after about 8 hours. During the first 2-3 minutes, water penetrates the dead tissues of fruit and seed coats[2]. Since only those parts of the seed which are in a state of imbibition are capable of reacting to light, the fact that photosensitivity manifests itself as early as 5 to 8 minutes after the inception of imbibition would indicate that photosensitivity is localized in the outermost living tissues of the seed. As the first manifestations of photosensitivity coincide with the beginning of imbibition by the endosperm and the embryo, it follows that responsiveness to light is not located in the coats but either in the endosperm, or the outer layers of the embryo, or in both. There are no grounds as yet for more precise localization.

In addition to instances of interaction between photo-and thermosensitivity reported elsewhere[1], the dependence of the light effect on temperature is indicated by the following facts.

(1) At higher temperature, a longer period of imbibition is needed before maximum photosensitivity is attained, while the actual level of sensitivity reached is lower (Figures 1 and 3).

(2) Germination of Grand Rapids seeds, which is strongly curtailed by inhibiting radiation at 26°C, is not affected by similar ardiation at 20°C (Table VII).

(3) Seeds of the varierty Progress, whose germination is not affected by inhibiting radiation at 26°C, (Table VI) succumbs to its effect when the temperature is raised to 29°C.

It has been shown by a number of workers that the stimulation induced by red light can be completely reversed by infrared. The relationship appears to be quantitative. in that the stimulating effect of a given amount of energy represented by a certain number of quanta of red light is counterbalanced by a measurable amount of energy or a number of quanta of infrared. The reversibility is complete when infrared follows immediately the application of red. When there is a time lapse between the applications, the reversibility is a function of the duration of the interval, and goes down to nil after about 10 hrs. It appears that whatever physiological process is involved in the stimulation of germination by red light, its fixation proceeds rather slowly.

Although sensitivity to white light decreases considerably after 8 hrs. of imbibition, it is still in evidence even after 12 hrs. Thus lettuce seeds do not seem to be subject to complete dark-dormancy, in contrast to other photoblastic seeds[9]. It appears that the process stimulated by red light remains in a state of metastable equilibrium for a considerable time.

The observations outlined above suggest the following general picture.

We assume that germination depends on a certain process or processes *P*. It is as yet too early to speculate on the physiological nature of *P*, but it is obviously set afoot by imbibition. provided that certain conditions are fulfilled.

These conditions may amount to *either* the elimination of a barrier *A*, or the presence of some substance A^+, or both. As long as *P* has not proceeded beyond a certain point, it can be stopped either by the disappearance of A^+or the re-establishment of *A*. As proposed in an earlier paper[10], *A* might be a dye with an absorption peak around 600 mμ. For the sake of convenience in subsequent discussion the suggested formulation is briefly restated.

$$A + h\nu \rightarrow A^* \qquad (1)$$

A^* loses an excired electron to an electron trap.

$$A^* \rightarrow A^+ + e^- \qquad (2)$$

A^+ can be formed by processes other than irridation, such as the reaction of oxygen with the dye molecule.

$$A + O_2 \rightarrow A^+ \ldots\ldots {}^-O^2 \qquad (3)$$

The process of formation of A^+ can be reversed in different ways.

The trapped electron e — can be freed from its trap by irradiation with infrared

$$A^+ + \bar{e} + h\nu \rightarrow A \qquad (4)$$

An increase in temperature could supply the required energy of activation for the liberation of the electron and the reformation of *A*. The energy requirement of the two back reactions is apparently not identical. In either case *P* would be stopped and germination inhibited.

This scheme[10] would account for the stimulation of germination by red light and its reversibility in response to infrared, in conformity with (1), (2) and (4). An acceptable explanation is also provided for the irreversibility of the process after the lapse of a certain period as well as for validity of the product law. Some insight is also gained into the role played by the endosperm in the case of lettuce seed, and by the seed and fruit coats of other seeds endowed with positive photoblasticity. Most authors[9] agree that these coats inhibit the normal gas exchange, i.e. either the intake of O_2, or the release of CO_2, or both. If the coats are removed, germination proceeds normally even in the dark.

Thus in terms of the proposed formulation, reaction (3) takes place after removal of the coats. In the presence of the coats, the reaction is precluded or only develops to an insufficient extent. In this case germination can be secured only with aid of reactions (1) and (2), i.e. upon irradiation with stimulating light. When the coats are off, infrared light no longer produces inhibition, as reaction (3) cannot be reversed by irradiation.

The suggested scheme also provides an explanation for the fact that, at 26°C, the germination of Progress seeds is independent of irradiation and cannot be inhibited by infrared. As will be shown in a forthcoming paper, the endosperm of Progress, as opposed to that of Grand Rapids, does not hinder the gas exchange and, therefore, does not interfere with reaction (3) at 26°C.

The suggested approach also makes it possible to explain the fact that raising the temperature results in a lowering of photosensitivity. It appears that higher temperatures upset the equilibrium between the light reaction (1) and the related thermal back reaction (2). By favouring the thermal process, high temperatures result in a decrease of photosensitivity.

REFERENCES

1. EVENARI, M., 1952, *Pal. Jour. Bot., Jer. Ser.*, 5, 138.
2. EVENARI, M. and NEUMANN, G., 1952, *Bull. Res. Counc. Of Israel*, 2, 75.
3. FLINT, L. H., 1934, *Sci.*, 80, 38.
4. FLINT, L. H. and MCALLISTER, 1935, *Misc. Coll.*, 94,1-11
5. FLINT, L. H. and MCALLISTER, 1937, *Smiths. Misc. Coll.*, 96, 1-8.
6. BOWEN, E. J., 1944, *Chemical Aspects of Light*, Oxford University Press, p. 280.
7. MEISCHKE, D., 1936, *Jahrb. Wiss. Bot.*, 83, 359.
8. RESUEHR, B., 1939, *Planta*, 30, 471.
9. EVENARI, M., The Effect of Visible Radiation upon Germination, in *Radiation Biology*, McGraw Hill and Co., New York (in press).
10. EVENARI, M. and STEIN, G., 1935, Experientia, 9, 94.

TABLE I

Effect of irradiation through different filters on the germination of lettuce seeds

Variety Grand Rapids. Temperature 26°C.

Number and colour of Wratten filter		Range of transmission	Region of maximum transmission of visible light (mμ)	*G.I.*	*G.I.(R)*
29	red	610—700	700	3.68	1.24
70	dark red	650—700	700	3.26	0.73
16	yellow-orange	520—700	660—700	3.31	1.26
9	yellow	470—700	600—700	3.10	1.25
34	red-violet	400—490	420	2.70	—
		640—700	700		
88 a	infrared	—	—	0.49	0.38
89 a	dark red	680—700	700	0.61	0.21
75	blue-green	460—530	490	0.58	0.32
54	green	510—570	550	0.53	0.37
50	dark-blue	400—490	460	0.59	0.23
49	blue	400—510	450	0.63	0.40
45	blue	430—540	480	0.70	0.63
47	blue	400—530	440	0.76	0.58
62	green	510—570	540	0.77	0.29
74	green	510—570	530	0.94	0.34
58	green	480—630	520	1.00	1.08
61	light green	490—610	520	0.99	0.91
60	green	450—610	520	0.95	1.05
44	blue-green	400—570	490—500	1.16	0.97

TABLE II

Infrared transmission of different filters (percent)

Number of Wratten filter	at mμ 700	720	740	760	780	800
45	0	24	70	88	89	91
47	0	0	3	18	45	64
49	0	0	0	8	38	67
50	0	0	2	18	46	66
54	2	13	45	66	81	88
58	1	1	1	1	2	4
60	4	5	5	6	8	14
61	0	0	0	0	0	0
62	1	24	73	96	87	90
74	0	1	0	3	27	56
88a	0	0	26	68	84	88
89a	19	67	83	87	88	89

TABLE III

Effect on germination of blue-filter (Wratten No. 45) in relation to infrared-absorbing solution and pre-treatment with stimulating radiation (through Corning glass red filter No. 245)

Variety Grand Rapids remperature 26°C. Light intensity 250 F.C. Irradiation after 2 hours of imbibition through red filter for 30 seconds, followed immediately by irradiation through blue filter (with or without solution) for 10 minutes.

Filter combination	Germination percentage	Filter combination	Germination percenage
Filter No. 45	12±1.2	Dark Control	35±4.7
Filter No. 45 after red	35±6.4	Red Control	79±2.8
Solution+filter No. 45	32±5.1	Solution only	45±6.0
Solution+filter No. 45 after red	79±6.2		

TABLE IV

Effect on germination of blue filter (Wratten No. 47) in relation to infrared-absorbing solution and pre-treatment with stimulating radiation (through Corning glass red filter No. 245)

Variety Grand Rapids. Temperature 26°C. Light intensity 250 F.C. Time intervals and periods as in Table III. Amounts of light equivalent to those in Table III.

Filter Combination	Germination percentage	Filter Combination	Germination percenta
Filter No. 47	21±4.2	Solution+filter No. 47 after red	74±2.8
Filter No. 47 after red	50±5.1	Dark control	37±3.6
Solution+Filter No. 47	35±3.5	Red control	73±5.0

TABLE V

Effect of decoating on the response of germination to irradiation with an infrared-transmitting filter (wratten No. 47) at 26°C.

Variety Grand Rapids. Light intensity 250 F.C. Irradiation through the blue filter was applied after 2 hours imbibition for 4 minutes.

Condition of seeds	Irradiation	Germination percentage
Decoated	Dark	49±7.9
Control	Dark	28±4.2
Decoated	Filter No. 47	45±5.8
Control	Filter No. 47	6±2.7

TABLE VI

Effect of irradiation through infrared-transmitting filters on the germination of variety Progress at 26°C.

Light intensity 250 F.C. Irradiation was applied after 2 hours of imbibition for 4 minutes through Filter No. 47. In the case of the other Wratten filters used, the duration of irradiation was adjusted to ensure equivalent amounts of light.

Radiation	Germination percentage	Radiation	Germination percentage
Filter No. 50	97±1.2	Filter No. 47	99±0.7
Filter No. 49	96±1.3	Dark Control	96±1.0

TABLE VII

The effect of irradiation through an infrared-transmitting filter on the germination of the variety Grand Rapids at 20°C.

Light: intensity 250 F.C. Irradiation was applied for 4 minutes through Wratten filter No. 47, after 2 and 4 hours imbibition respectively.

Condition of seeds	Irradiation	Germination percentage
	Dark control	84
After 2 hrs. soaking	Filter No. 47	87
After 4 hrs. soaking	Filter No. 47	81

TABLE VIII

Effect on germination of the time interval between stimulating irradiation and subsequent application of inhibiting radiation

Variety Grand Rapids. Temperature 26°C . Light intensity 250 F.C. Irradiation after 2 hours of imbibition throgh red filter (Corning glass No. 245) for 30 seconds, followed at varying intervals by irradiation through a blue filter (Wratten No. 47) for 4 minutes.

Treatment	Time after application of red filter	Germination percentage	G.I.
Filter No. 47	directly	22	0.3
"	6 hrs.	59	0.7
"	8 hrs.	66	0.8
"	10 hrs.	73	0.9
Red filter only	—	80	1.0
Dark control	—	26	—

TABLE IX

Effect on germination of white radiation applied after varying periods of imbibition

Variety Grand Rapids. Temperature 26°C. Light intensity 250 F.C.

Duration of irradiation (sec.)	Germination percentage Duration of imbibition before irradation 48 hrs.	72 hrs.
5	1	2
10	9	8
15	15	9
20	24	11
30	21	11
40	30	22
50	41	27
60	34	22
120	41	30
--	2	3

TABLE X

Effect on germination of different periods of irradiation with white light of varying intensity

Variety Grand Rapids. Temperature 26°C. All treatments were applied after 2 hours of imbibition.

Light intensity	1000 F. C.		250 F. C.		62 F. C.		31 F. C.	
F.C. sec.	%	*G.I.*	%	*G.I.*	%	*G.I.*	%	*G.I.*
1500	54	3.6	39	2.6	64	4.3	46.5	3.2
3000	70	4.6	56	3.7	—	—	75	5.1
6000	81	5.4	81.5	5.4	—	—	92.5	6.1
9000	85	5.6	87.5	5.8	—	—	91.5	6.1

Light intensity	500 F.C.		250 F.C.		125 F.C.		62 F.C.	
F.C. sec.	%	*G.I.*	%	*G.I.*	%	*G.I.*	%	*G.I.*
1250	45.5	1.8	25.5	1.1	37	1.4	24	1.0
2500	51.5	2.2	55	2.1	49	1.9	45	1.7
5000	71.5	2.8	79.5	3.1	72	2.8	75	2.9
7500	81.5	3.2	89.5	3.4	80.5	3.1	86.5	3.3

Light intensity	500 F.C.		250 F.C.		125 F.C.	
F.C. sec.	%	*G.I.*	%	*G.I.*	%	*G.I.*
1250	60	2.1	49.0	1.7	36	1.5
2500	61.5	2.7	61	2.2	58	2.1
5000	81.5	2.9	88.5	3.1	88	3.2
7500	89	3.2	93.5	3.3	89.5	3.8

TABLE XI

Effect on germination of different periods of stimulating radiation (Corning glass filter No. 245) of varying intensity.

Variety Grand Rapids. Temperature 26°C. All treatments were applied after 2 hours of imbibition.

Light intensity	1000 F.C.		500 F.C.		250 F.C.	
F.C. sec.	%	*G.I.*	%	*G.I.*	%	*G.I.*
500	—	—	42	1.39	41	1.35
2000	72.5	3.25	70.7	3.15	73.5	3.30
4000	82.5	2.89	89	3.12	75.8	2.66

Ligh intensity	125 F.C.		62 F.C.		31 F.C.		15 F.C.	
F.C. sec.	%	*G.I.*	%	*G.I.*	%	*G.I.*	%	*G.I.*
62	—	—	33.5	0.97	31	1.27	—	—
125	27	0.78	29.5	0.86	—	—	—	—
250	37	1.22	37	1.22	26.3	0.76	—	—
500	49.5	1.63	42.5	1.40	42	1.39	—	—
2000	75.5	3.37	67.3	3.00	65.6	2.93	72.5	3.25
4000	85.5	3.00	83	2.89	—	—	—	—

TABLE XII

Effect on germination of different periods of inhibiting radiation of varying intensity following directly upon application of stimulating radiation.

Variety Grand Rapids. Temperature 26°C. Stimulating radiation was applied after 2 hours imbibition by passing white light at 200 F.C. for 32 seconds through a red Corning glass filter No. 245. Inhibiting radiation was obtained by means of Wratten filter No. 47. Germination index *G.I.* (*R*) is related to the germination percentage obtained with the use of a red filter alone.

Light intensity	250 F.C.		125 F.C.		62.5 F.C.	
F.C. min.	%	*G.I.*(*R*)	%	*G.I.*(*R*)	%	*G.I.*(*R*)
250	—	—	82	1.0	81	1.0
500	—	—	73	0.9	75	0.9
1250	40	0.5	41	0.5	42	0.5
2500	25	0.3	28	0.3	—	—

SUMMARIES Vol. III No. 1-2

OLLENDORFF, F.

A Contribution to the Treatment of the Relativistic Keplerian Motion Bull. Res. Counc. of Israel, 1953, **3**, 25.

The paper deals with the relativistic laws of motion of an electron approaching a fixed electric charge from infinity with a given initial velocity. The relations resulting from the Lagrangian of the problem give, by direct integration, the equations of momentum and energy. On this basis the kinematic equation of the electron path is obtained and is simply integrated. In the case that the electron is approaching a negative charge the resulting path differs only quantitatively from the classic Kepler hyperbola, on the other hand if the electron is attracted by a positive charge, two quite different possibilities exist. The path of the controlled electron is similar to that of the classical Kepler theory only when the initial velocity is higher than a critical value, which depends upon the direction of approach. When the initial velocity is smaller than the critical value, the electron path becomes a spiral, along which the electron approaches the center of attraction. Comparison of this relativistic solution with that of the classical theory shows the surprising fact that the relativistic effect is the greater the smaller the initial velocity of the electron. On the basis of the above results, Rutherford's theory of α-particle scattering remains valid; however, the treatment of ion recombination in gases requires fundamental revision.

BARUCH, J. and LOW, W.

The Dielectric Constant of 'Free' and 'Bound' Water at Microwave Frequencies, Bull. Res. Counc. of Israel 1953, **3**, 31.

Microwave dielectric measurements on distilled water and water in crystals, hygroscopic salts, gels, and hydrated organic molecules are analyzed. It is shown that crystalline water and water contained in hygroscopic salts show no dispersion in the microwave region, whereas aq. gels and silica gel do. In most hygroscopic salts there is a reaction from rotationally 'free' to 'bound' water. The velocity of the reaction is a function of the temperature and of the amount of water already bound. Results on gelatin and thixotropic gels show that that most of the water is rotationally 'free' and indicate that the structure of the gel is primarily due to the solute. Measurements of the dielectric constant and loss factor of gelatin as a function of temperature and of yeast as a function of water content are reported and analyzed.

HIRSHFELD, F. L. and SCHMIDT, G. M. J.

Geiger-counter Measurements of Single-Crystal Bragg Reflections. The Geometrical Problem. Bull. Res. Counc. of Israel, 1953, **3**, 37.

The accuracy attainable by the use of Geiger-counter data in x-ray crystallographic structure analyses makes desirable the development of a Geiger-counter spectrometer for the measurements of integrated Bragg reflections from single crystals. Many different combinations of crystal and counter motions are possible for scanning the reciprocal lattice, of which several offer special advantages in simplicity of design or convenience of operation. Three methods are described in detail, with equations defining the orientations of the crystal and of the counter tube for each Bragg reflection.

For measuring integrated intensities, it is convenient to use a convergent x-ray beam rather than a rotation or oscillation of the crystal. With this device, a Lorentz factor is introduced that depends on the angle between the reflected beam and the plane of convergence. Expression for this factor are given corresponding to the different scanning methods described.

PATAI, S. and RAJBENBACH, L.

Catalysed Solid-Solid Oxidation Reactions, Bull. Res. Counc. of Israel, 1953, 3, 46.

The catalytic action of various salts on the heterogeneous (solid-solid) oxidation of carbon black, nuchar, graphite and different poluymers by potassium perchlorate was studied by measuring the amount of carbon dioxide evolved from the samples at intermediate reaction temperatures (320°—450°). The reaction curves obtained with the three forms of carbon have been found to conform to the kinetic equation $kt = [1 - \sqrt[3]{(100 - x)}/100]^2$. Possible mechanisms of the catalysis by salts (especially halogenides) are discussed, and it is proposed that the catalyst takes part in the reaction as an oxygen carrier in the form of oxygenated intermediates.

BODENHEIMER, W. and GOLDSTEIN, M.

Simultaneous Micro-estimation of Carbon and Hydrogen in Organic Fluorine Compounds, Bull. Res. Counc. of Israel, 1953, 3, 53.

A process has been developed for the simultaneous micro-determination of carbon and hydrogen in fluorine-containing organic compounds. Lead dioxide is used as an absorbent for the volatile fluorine compounds formed (SiF_4, HF). A formula is given for the correction of the hydrogen values which are increased by water liberated from the lead dioxide layer. The method has proven satisfactory for a wide range of compounds including substances that contain nitrogen, much fluorine and little or no hydrogen. It is expected that the method can be extended into a simultaneous determination of carbon, hydrogen and fluorine, at least in compounde which do not contain nitrogen.

GALLILY, I .

On the Absorption of Active Gases fom Streaming Air, Bull. Res. Counc. of Israel, 1953, 3, 56.

A convenient method is described for testing the absorptive efficiency of the gas mask, or any other bed of an absorbent, with respect to chloride, under various conditions of initial concentration, relative humidity and rate of flow. The effect of temperature can be investigated easily by attaching a suitable pre-heater to the air line. Other gases may replace chlorine if the gas supply line and the analyzer are altered appropriately.

REINER, M.

On Volume — Viscosity Bull. Res. Counc. of Israel, 1953, 3, 68.

Under isotropic stress all materials, whether solids or liquids, behave in the same manner, namely exhibit elasticity. They must therefore also exhibit solid volume viscosity (ζ_s) as introduced by Kelvin (1865). This makes the mean pressure of a liquid

$$p_m = -p_{aa}/3 = -(ke_v + \zeta_s \dot{e}_v)$$

where e_v is the recoverable volume-strain, different from thermodynamic static pressure p. However, in general, there will be in a liquid also irrecoverable volume flow f_v connected with p_m by $f_v = -p_m/\zeta_l$ where ζ_l is the coefficient of liquid volume viscosity. This is connected with λ_T, Trouton's coefficient of viscous traction, and η, the coefficient of shear viscosity, by $\lambda_T = 9\ \zeta_l \eta\ (3\ \zeta_l + \eta)$.

From this, the volumetric rheological equation of the general viscous liquid is $p_m + \dot{p}_m(\zeta_s + \zeta_l)/k = -\zeta_l(d_v + \zeta_s \dot{d}_v/k)$ where d_v is the cubical dilatation of the liquid. One must accordingly distinguish between *two* coefficients of volume viscosity, one (ζ_s) connected with recoverable volume-*strain*, the other (ζ_l) with irrecoverable volume-*flow*. In general, the liquid will show retardation of elastic response, the time of retardation being $\tau_{ret} = \zeta_s/k$, and relaxation of elastic stresses, the time of relaxation being $\tau_{rel} = (\zeta_s + \zeta_l)/k$. For the Stokesian liquid $\zeta_s = 0$, $\zeta_l = \infty$, $\tau_{rel} = 0$ and $\tau_{rel} = \infty$. A mechanical model consisting of an elastic spring and a viscous dashpot coupled in parallel, both with another dashpot coupled in series, offers a suitable representation of the volumetric behaviour of thr viscous liquid.

BERGMANN, E. D. and LOEWENTHAL, H. J. E.

The Photochemical Dehydrogenation of Bianthrone Derivatives, Bull. Res. Counc. of Israel, 1953, **3**, 72.
The known data on the photochemical dehydrogenation of bianthrones to helianthrones and naphthodianthrones are surveyed. A mechanism is suggested for this curious reaction, and the possible effect of the geometrical structure of the bianthrone on its course is discussed.
The influence of the position and nature of substituents on the photochemical dehydrogenation of bianthrones has been investigated. Whilst 4,5'-*dimethyl*-bianthrone remains unchanged, the corresponding *dibromo*-compound loses hydrogen bromide and gives naphthodianthrone.

BOBTELSKY, M. and GRAUS, B.

Thorium Tartrate Complexes, their Composition, Structure and Behaviour, Bull. Res. Counc. of Israel, 1953, **3**,82. The phenomena observed may be accounted for as follows. Thorium nitrate with sodium tartate gives a soluble complex [$ThTa_2$] (pH ~ 3.0) and an insoluble compound [ThTa]$_2$ (pH ~ 2.0). The latter is redissolved in excess of tartrate through the formation of the complex [$ThTa_2$]. With one equivalent of sodium hydroxide per one [$ThTa_2$], a soluble complex [ThTa'Ta] is obtained (pH ~ 5.0). With two equivalents of sodium hydroxide the soluble complex [ThTa'']^o (pH ~ 8.0) is obtained. The latter is the only complex which exists in a thorium tartrate solution at pH $\geq$8.0. The insoluble compound [ThTa]$_2$ is soluble in an excess of thorium, probably through the formation of the cation complex [Th_2Ta] which exists at low pH $\sim$ 2.0).

GLASNER, A. and MAKOVKY, A.

The Thermal Decomposition of Guanidine Perchlorate, Part II. Kinetics, Bull. Res. Counc. of Israel, 1953, **3**, 89.

PELCHOWITZ, Z. and BERGMANN, E. D.

A Total Synthesis of Pyrene, Bull. Res. Counc. of Israel 1953, 3, 91.
The reaction of 2,6,2',6,'-tetra (bromomethyl)-biphenyl (VII) with lithium phenyl gives 1,2,6,7,-tetrahydropyrene (VIII). The ultraviolet spectrum of (VIII) is discussed.

SZMUSZKOVICZ, J. and BERGMANN, E. D.

Syntheses with Cyclohexen-1-Aldehyde, Bull. Res. Counc. of Israel, 1953, **3**, 93.

HEIMANN, H. and RATNER, R.

Cation Exchangers from Olive Pits, Bull. Res. Counc. of Israel, 1953, **3**, 96.
A cation exchanger was prepared from olive pits by treatment with concentrated sulfuric acid. The groups active in exchange are mainly carboxylic ones (-COOH) and to a lesser degree sulfonic groups (-SO_3H).
They were determined by fixation of ammonia gas (giving the total acid groups) and estimation of total S (giving the maximum value for sulfonic groups). The exchange capacity was measured for work on the sodium cycle and on the hydrogen cycle as well.

BERGMANN, F. and VROMEN, S.

The Meerwein Reaction of β -Nitrostyrene, Bull. Res. Counc. of Israel, 1953 3, 98.

1. β -Nitrostyrene reacts with aryl diazoacetates, in the presence of cupric chloride, to form substituted stilbenes.

2. In the reaction with *p*-nitrophenyl diazoacetate a ketone was obtained — in addition to *p*-nitrostilbene — which is most probably benzyl *p*-nitrophenyl ketone.

3. The results are different from those obtained in the Meerwein reaction of cinnamic acid. A possible explanation is derived from the assumption that in the intermediate radical enolization of the nitro group permits an intramolecular shift of hydrogen. A nitroparaffin is thus obtained, which may either yield a stilbene by elimination of HNO_2 or undergo the Nef reaction to give a ketone.

BLANK I., MAGER J. and BERGMANN, E. D.

Diethyl Oxalo-fluoroacetate. Bull. Res. Counc. of Israel, 1953, 3, 101.

This paper is the first in a series of studies dealing with the fluorosubstituted components of the *Krebs* cycle. Diethyl and di-*t*-butyl oxalo-fluoroacetate have been prepared and their properties have been investigated. The keto-esters are practically not enolised· their hydrolysis leads so quickly to oxalic acid that the desired free keto-acid could not be prepared in pure form. The diethyl ester is not toxic to animals, but is a potent inhibitor of bacterial growth.

SPRINZAK, Y.

Carbon-benzylation by Means of Benzyl Alcohol, Bull. Res. Counc. of Israel, 1953, 3, 106.

Fluorene and its derivatives are readily benzylated in the 9-position on heating with benzyl-alcoholic potassium hydroxide in presence of traces of benzaldehyde. The derivatives tested include 2-methyl-, 2-bromo-, 2,7-dibromo-, 1,2,3,4-dibenzo- and 2-hydroxy-fluorene.

The course of the reaction has been shown to involve condensation of fluorene with benzaldehyde to form benzylidene-fluorene, followed by reduction of the latter to 9-benzylfluorene. The ease of reduction of benzylidene-fluorene under the conditions of the reaction is attributed to the polar character of the semicyclic bond in this compound.

BERENBLUM, I.

Some Aspects of Carcinogenesis, Bull. Res. Counc. of Israel, 1953, 3, 106.

SHELESNYAK, M. C.

The Influence of Post-Stimulation Time-interval upon the Effective Inhibition by Benadryl of Deciduoma Formation, Bull. Res. Counc. of Israel, 1953, 3, 112.

Both uterine horns of 48 young adult pseudopregnant rats were traumatized, mechanically by scratching, or chemically by histamine injection, in order to provoke decidual cell formation. At various intervals from one to 48 hours after traumatization, Benadryl was introduced into one lumen, in doses of 1, 2, or 10 mg/0.1 ml.

Inhibition or suppression of the decidual reaction was effected even when Benadryl was introduced as late as from 18 to 48 hours. The larger dose of Benadryl was effective after longer intervals.

BODENHEIMER, F. S.

The Concept of Biotic Organization in Synecology, Bull. Res. Counc. of Israel, 1953, 3, 114.

VOLCANI, R.

Seasonal Variations in Spermatogenesis of Some Farm Animals under the Climatic Conditions in Israel, Bull. Res. Counc. of Israel, 1953, **3**, 123.

DAVIES, A. M. and YOSHPE-PURER, Y.

Aedes aegypti *as a Vector of West Nile Virus*, Bull. Res. Counc. of Israel, 1953, **3**, 127.
Evidence is presented that in addition to *Aedes aegupti* being capable of transmitting the West Nile virus in the laboratory, multiplication of the virus occurs within the body of the mosquito, thus indicating that this mosquito acts as a true biological vector.

PLAUT, M., SELCBUCH, B. and GUGGENHEIM, K.

Nutritional Value and Baking Properties of Carob Germ Flour, Bull. Res. Counc. of Israel, 1953, **3**, 129.

PICARD, L.

Disharmonic Faulting — A Tectonic Concept, Bull. Res. Counc. of Israel, 1953, **3**, 132.
The fault patterns of the Jordan Araba graben are described, emphasising differences between superstructure and substructure, i.e. the disharmonic faulting, which is a fundamental concept in tafrogenic tectonics.

EVENARI, M. and NEUMANN, G.

The Germination of Lettuce Seeds, III. The Effect of Light on Germination, Bull. Res. Counc. of Israel, 1953, **3**, 136.

At 26°C, the germination of seeds of the lettuce variety Grand Rapids was found to be stimulated by red and inhibited by infrared radiation. If infrared was applied *immediately* after irradiation with red, the stimulation of germination induced by the red radiation was completely nullified. However, the greater the time allowed to lapse before the infrared application, the smaller its counteracting effect.

The inhibiting effect of blue and green filters was found to be due to their transmission of infrared, while the stimulating effect of yellow filters was accounted for by their transmission in the red region.

The germination of Grand Rapids seeds at 20°C, and of decoated seeds of the same variety at 26°C, was not inhibited by infrared radiation.

At 26°C the seeds of the variety Progress were shown to be entirely non-photoblastic, whereas at 29°C their germination was inhibited by infrared.

In Grand Rapids seeds, photosensitivity set in after 5-8 minutes of soaking. Photosensitivity attained its maximum at 26°C after 8 hrs., 3 hrs. and 1 hr. from the inception of imbition, for white, red and infrared light respectively. After 72 hours imbibition, the seeds still reacted to white light, though their photosensitivity was greatly reduced. Photosensitivity was found to be a function of temperature.

In the case of red and infrared light, the product law was found valid for the whole range investigated: for white light, its validity was confined to 2500 9000 F.C. sec.

A theoretical scheme, attempting coordination of the observed phenomena, is proposed.

WEIZMANN MEMORIAL LECTURES

In commemoration of the death of DR. CHAIM WEIZMANN, one year ago, a series of scientific lectures and symposia will be held at the Weizmann Institute of Science, Rehovot.
The series, whose programme is given below, will be concluded by the WEIZMANN MEMORIAL LECTURES on Monday, December 7, 1953 by PROF. SIR ROBERT ROBINSON.
All lectures will subsequently be published.

Monday, November 2, 1953
10.00 a.m.

Chairman: ISRAEL DOSTROVSKY, *Weizmann Institute of Science, Rehovot*
HERMAN F. MARK, *Polytechnic Institute of Brooklyn*
Progress in the Field of Plastics, Rubbers and Fibres (with demonstration)

2.30 p.m.

SYMPOSIUM ON BIOLOGY

Chairman: ERNST CHAIN, *Instituto Superiore di Sanita, Roma*
F. PEYTON ROUS, *Rockefeller Institute of Medical Research, New York*
Natural History of Cancer.
I. BERENBLUM, *Weizmann Institute of Science, Rehovot*
The Biological Mechanism of Carcinogenesis
M. C. SHELESNYAK, *Weizmann Institute of Science, Rehovot*
The Mechanism of Nidation in the Mammalian Uterus
L. SACHS, *Weizmann Institute of Science, Rehovot*
The Genetic Analysis of Evolution

Tuesday, November 3, 1953
11.30 a.m.

Dedication of the Department of Experimental Biology (Isaac Wolfson Building)
Laying of the corner stone of the Institute of Physics

3.30 p.m.

Conferring of Honorary Fellowships of the Weizmann Institute of Science upon *Professor Niels H. Bohr, Professor Ernst B. Chain, Professor Hermann F. Mark, Professor Linus C. Pauling, and Dr. F. Peyton Rous.*
Lecture:
NIELS H. BOHR, *Institute for Theoretical Physics, Copenhagen*
Physics and Philosophy

Wednesday, November 4, 1953
9.00 a.m.

SYMPOSIUM ON POLYMERS AND PROTEINS

Chairman: F. PEYTON ROUS, *Rockefeller Institute of Medical Research, New York*
HERMAN F. MARK, *Polytechnic Institute of Brooklyn*
Progress in the Study of Macromolecules in Solution

AHARON KATCHALSKY, *Weizmann Institute of Science, Rehovot*
Polyelectrolyte Gels
LINUS C. PAULING, *California Institute of Technology, Pasadena*
The Structure of Proteins

2.30 p.m.

SYMPOSIUM ON MICROBIOLOGY AND CHEMISTRY

Chairman: SAUL ADLER, *Hebrew University — Hadassah Medical School, Jerusalem*
ERNST B. CHAIN, *Instituto Superiore di Sanita, Roma*
Intermediary Carbohydrate Metabolism
EPHRAIM KATCHALSKI, *Weizmann Institute of Science, Rehovot*
The Action of Proteolytic Enzymes on Poly-α-Amino Acids
SHLOMO HESTRIN, *Hebrew University — Hadassah Medical School, Jerusalem*
Synthesis and Degradation and Some Biological Properties of Intercellular Polysaccharides

Thursday, November 5, 1953
9.00 p.m.

SYMPOSIUM ON PHYSICS

Chairman: HERMAN F. MARK, *Polytechnic Institute of Brooklyn*
NIELS H. BOHR, *Institute for Theoretical Physics, Copenhagen*
Atoms, Molecules and Nuclei
GIULIO RACAH, *The Hebrew University of Jerusalem*
Angular Correlation of Nuclear Radiations
AAGE BOHR, *Institute for Theoretical Physics, Copenhagen*
Nuclear Rotational States
STEFAN ROZENTAL, *Institute for Theoretical Physics, Copenhagen*
The Work of the Institute for Theoretical Physics in Copenhagen

3.00 p.m.

Chairman: B. M. BLOCH, *Weizmann Institute of Science, Rehovot*
LINUS C. PAULING, *California Institute of Technology, Pasadena*
Haemoglobin in Health and Disease

NOTICE TO CONTRIBUTORS (cont'd)

References

Articles *

References are to be cited in the text by the author's name and date of publication in parenthesis, e.g., (Taylor, 1932). If the author's name is already mentioned then just the year, appears in the parenthesis, e.g., ... found by Taylor (1932)... They are to be arranged in alphabetical order and the following form should be used:

3. TAYLOR, G. I., 1932, *Proc. R. Soc.* London, **A138**, 41.

Book references should be prepared according to the following order:

4. JACKSON, F., 1930, *Thermodynamics*, 4th ed., Wiley, New York.

The title of a paper will appear in the references only if it has been published solely in a local Hebrew journal. This is printed in regular type and is indicated by double inverted commas.

Letters to the Editor

In Letters, references are to be cited in the text by numbers, e.g., Taylor[3] and are to be arranged in the order in which they appear in the text.

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* In this special issue the form indicated for *Letters to the Editor* has been used.

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